

THE CLASSICAL LIMIT OF QUANTUM OBSERVABLES IN THE CONSERVATION LAWS OF FLUID DYNAMICS*

PETR PLECHÁČ[†], MATTIAS SANDBERG[‡], AND ANDERS SZEPESSY[§]

Abstract. In the classical work by Irving and Zwanzig [J.H. Irving and R.W. Zwanzig, *J. Chem. Phys.*, 19, 1173–1180, 1951] it has been shown that quantum observables for macroscopic density, momentum and energy satisfy the conservation laws of fluid dynamics. In this work we derive the corresponding classical molecular dynamics limit by extending Irving and Zwanzig’s result to matrix-valued potentials for a general quantum particle system. The matrix formulation provides the classical limit of the quantum observables in the conservation laws also in the case where the temperature is large compared to the electron eigenvalue gaps. The classical limit of the quantum observables in the conservation laws is useful in order to determine the constitutive relations for the stress tensor and the heat flux by molecular dynamics simulations. The main new steps to obtain the molecular dynamics limit are: (i) to approximate the dynamics of quantum observables accurately by classical dynamics, by diagonalizing the Hamiltonian using a nonlinear eigenvalue problem, (ii) to define the local energy density by partitioning a general potential, applying perturbation analysis of the electron eigenvalue problem, (iii) to determine the molecular dynamics stress tensor and heat flux in the case of several excited electron states, and (iv) to construct the initial particle phase-space density as a local grand canonical quantum ensemble determined by the initial conservation variables.

Keywords. conservation laws; stress tensor; heat flux; molecular dynamics; Weyl quantization.

AMS subject classifications. 35L65; 35Q70; 82C10; 81Q20.

1. The purpose of the work and the results

The macroscopic conservation laws for mass, momentum and energy form the basis of continuum fluid mechanics. These conservation laws are formulated in terms of the stress tensor and the heat flux. In order to form a closed system constitutive relations for the stress tensor and the heat flux are used. Such constitutive relations can be determined approximately from measurements or from molecular dynamics simulations. In both cases one seeks approximations of the stress tensor and the heat flux as functions of the density, momentum and energy and their derivatives. The molecular dynamics formulation requires derivation of the stress tensor and the heat flux as functions of the particle dynamics. The derivation of such functional relations is the focus of this work.

The stress tensor and the heat flux were first derived by Irving and Kirkwood, [5], from molecular dynamics systems based on interaction with scalar pair potentials and has later been modified by Noll, [14], and Hardy, [4]. These formulations have been used frequently to numerically determine the constitutive relations, cf. [3]. For instance, the works [18] and [19] include comparisons of different methods to numerically determine the stress tensor in molecular dynamics simulations.

Already in 1951 Irving and Zwanzig, [6], showed that quantum observables for the density, momentum and energy satisfy the conservation laws and derived observables

*Received: September 13, 2018; Accepted (in revised form): July 8, 2019. Communicated by Jianfeng Lu.

The research of A.S. and M.S. was supported by Swedish Research Council 621-2014-4776. The research of P.P. was supported by ARO MURI Award No. W911NF-14-024.

[†]Department of Mathematical Sciences, University of Delaware, Newark, DE 19716, USA (plechac@udel.edu).

[‡]Institutionen för Matematik, Kungliga Tekniska Högskolan, 100 44 Stockholm, Sweden (msandb@kth.se).

[§]Institutionen för Matematik, Kungliga Tekniska Högskolan, 100 44 Stockholm, Sweden (szepessy@kth.se).

for the stress tensor and the heat flux. Since it is only at the quantum level the particle interaction is determined from fundamental principles; their result provides a solid foundation for the basic conservation laws in continuum mechanics. The property that the observables for the density, momentum and energy satisfy the conservation laws does not mean that a closed system of conservation laws is derived, since the derived stress tensor and the heat flux are not determined as constitutive functions of the macroscopic conservation variables. Forming a closed system would include the additional step to determine constitutive functions of the conservation variables that approximate the data from molecular dynamics or measurements, which is not studied here.

Irving and Zwanzig used a quantum model with the Hamiltonian given by a sum of kinetic energy and scalar pair potential energy including all particles, i.e. both the nuclei and the electrons. The aim of this work is to extend the derivation by Irving and Zwanzig to a setting with a matrix-valued Hamiltonian consisting of a sum of the kinetic energy of the nuclei (times the identity matrix) and a matrix representing the electron kinetic energy, the electron-electron, electron-nuclei, and nuclei-nuclei interaction. The purpose of having a matrix for the electron part in the Hamiltonian is to replace the time evolution for the electrons by the Schrödinger electron eigenvalue problem. An advantage of including the electron part as a matrix-valued operator is that the classical limit, as the nuclei-electron mass ratio tends to infinity, has been derived rigorously, [16] and [7], and by knowing the classical limit the system can be simulated by ab initio molecular dynamics for nuclei with the potential generated by the electron eigenvalue problem. For instance, one may ask how the observables of the density, momentum, energy, stress tensor and heat flux are effected by the possibility of excited electron states and how these observables should be computed in molecular dynamics simulations. This question is answered in Theorem 5.2 by applying the classical molecular dynamics limit of quantum observables in [7]. The work [7] is for the setting of constant temperature in the canonical ensemble and shows, for example, how the potential is modified also when the difference of the excited and ground state electron eigenvalue is not large compared to the temperature.

The time evolution of the conserved quantum observables uses the ingenious observation by Irving and Zwanzig that, for an observable that is a polynomial of the degree at most two in the momentum coordinate, the commutator of the Hamiltonian operator and that quantum observable becomes equal to the Weyl quantization of the Poisson bracket. Combined with the observation that the observables for density, momentum and energy are polynomials of degree at most two in the momentum coordinate, the quantum observables therefore satisfy the same conservation laws as in the derivation based on classical particle dynamics by Irving and Kirkwood. However, in the case of matrix-valued potentials the commutator of the Hamiltonian and the quantum observables for mass, momentum and energy does not reduce to a Poisson bracket since the matrix-valued symbols do not commute in general. In this work we show that for a certain diagonalization, based on a nonlinear eigenvalue problem, these commutators are reduced to a quantization of corresponding Poisson brackets.

To define the energy observable the works [4-6, 14] use that the potential energy can be split into a sum of potential energies related to each particle as defined by pair interactions. In the matrix-valued case considered here the splitting is required for the eigenvalues of the matrix potential which is not a sum of pair potential interactions. Our splitting is instead obtained by using perturbation theory for eigenvalues.

The pair potential property is also used in the works [4-6, 14] to reduce forcing terms to divergence of a stress term. Such reduction has been obtained in [1] for general

potentials that are invariant with respect to translation and orthogonal transformations by changing to the coordinates depending on all pair distances. This change to the pair distance coordinates is also used here.

The compressible Euler equations have been derived from classical perturbed Newtonian particle dynamics using the relative entropy method in [15]. The classical Newtonian particle dynamics based on short range pair potential interactions is then weakly perturbed in two ways: to avoid unbounded velocities the kinetic energy is modified, for instance as relativistic, and to prove ergodicity with respect to Gibbs distributions the Hamiltonian dynamics is perturbed by a weak noise term that vanishes in the macroscopic hydrodynamic limit. The main accomplishment in [15] is to show that the density solving the Liouville equation that is initially close to a grand canonical Gibbs measure remains close to a grand canonical Gibbs measure at later time, so that the Gibbs measure determines the compressible Euler equations for all times, as long as the solution to the Euler equations remains smooth. The work [15] achieves the mathematically ambitious goal to derive a closed system of conservation laws from microscopic dynamics, which also requires additional assumptions and restricts to a setting with smooth classical solutions to the Euler equations. The Euler equations includes a pressure term that originates from microscopic particle forces. The relative entropy method has also been used to derive the compressible Euler equations, with a certain pressure term, in a scaling limit from a quantum system of fermions under an assumption of ergodicity of the quantum dynamics with respect to the Gibbs measure, see [13]. The objective in our work here is different from [15] and [13], in particular, we derive microscopic expressions for the stress tensor and the heat flux from a general quantum mechanical setting but we do not address the question of deriving a closed system of conservation laws from quantum mechanics.

We formulate the quantum mechanical model and the conservation laws in Section 2. In Sections 3 and 4 we review the derivations of the conservation laws from classical and quantum dynamics, respectively, following the works [4–6, 14], although reformulated in order to prepare for the new results in Section 5. These derivations are then used to obtain the matrix-valued extension of the quantum dynamics in Section 5. We derive the main result in Theorem 5.2, namely a classical molecular dynamics limit of the quantum observables in the conservation laws, under some assumptions on regularizations: the semiclassical analysis result requires L^2 bounded symbols, which is not satisfied in the canonical quantum formulation. The theorem therefore assumes that certain regularized L^2 -bounded symbols depend continuously on the regularization parameters. In Section 6 we present an approach for determining an initial phase-space density that matches the initial conservation variables locally. Following [1] we discuss in Section 7 the non-uniqueness question for the stress tensor.

In conclusion, the main result in this work is to formulate the quantum conservation laws using matrix-valued symbols and apply recent techniques from semiclassical analysis to determine the molecular dynamics stress tensor and heat flux in the case of several excited electron states. A new ingredient in the formulation is also to define the local energy density by partitioning a general potential, applying perturbation analysis of the canonical electron eigenvalue problem; previous work on molecular dynamics formulations of the conservation laws used empirical pair potentials, [4, 5, 14, 15]. As in [15] we construct the initial particle phase-space density as a local grand canonical quantum ensemble determined by the initial conservation variables.

We think that the present work is the first ab initio result that determines the stress and the heat flux in a molecular dynamics setting with several excited states and at any

temperature. Therefore we believe that this is a valuable first step for further study. For instance, it would be interesting to extend the result by determining conditions that imply the assumed continuous dependence on the regularization parameters.

2. Problem formulation

2.1. The quantum-mechanical model. We consider derivation of conservation laws from ab initio dynamics for which the starting point is the quantum mechanical model consisting of N nuclei (heavy particles or slow degrees of freedom) and J electrons (light particles or fast degrees of freedom). Each particle has a related position coordinate in \mathbb{R}^3 and a discrete spin coordinate. The spin coordinate $\bar{\sigma}_i$ for each electron takes the value in the set $\{-1/2, 1/2\}$, and similarly the spin coordinate σ_i for a nucleus can take values in a discrete set $\{-s, -s+1, \dots, s\}$, see [2, 10]. The quantum system at time t is then described by a wave function

$$\Phi(x^1, \sigma^1, x^2, \sigma^2, \dots, x^N, \sigma^N, \bar{x}^1, \bar{\sigma}^1, \bar{x}^2, \bar{\sigma}^2, \dots, \bar{x}^J, \bar{\sigma}^J, t) \in \mathbb{C},$$

with nuclei position coordinates $x = (x^1, x^2, \dots, x^N) \in \mathbb{R}^{3N}$ and electron position coordinate $\bar{x} = (\bar{x}^1, \bar{x}^2, \dots, \bar{x}^J) \in \mathbb{R}^{3J}$, and spin coordinates $\sigma = (\sigma^1, \dots, \sigma^N) \in \Sigma \equiv \{-s, -s+1, \dots, s\}^N$ and $\bar{\sigma} = (\bar{\sigma}^1, \dots, \bar{\sigma}^J) \in \bar{\Sigma} \equiv \{-1/2, 1/2\}^J$. The wave function is required to satisfy the Pauli exclusion principle which implies that it is anti-symmetric with respect to interchanging electron coordinates, namely

$$\Phi(\dots, \bar{x}^i, \bar{\sigma}^i, \dots, \bar{x}^j, \bar{\sigma}^j, \dots, t) = -\Phi(\dots, \bar{x}^j, \bar{\sigma}^j, \dots, \bar{x}^i, \bar{\sigma}^i, \dots, t)$$

and similarly identical fermion nuclei are also anti-symmetric while identical boson nuclei are symmetric with respect to its nucleon coordinates, see [2, 10]. We note that

$$\frac{|\Phi(x, \sigma, \bar{x}, \bar{\sigma}, t)|^2}{\sum_{\sigma \in \Sigma} \sum_{\bar{\sigma} \in \bar{\Sigma}} \int_{\mathbb{R}^{3(N+J)}} |\Phi(x, \sigma, \bar{x}, \bar{\sigma}, t)|^2 dx d\bar{x}}$$

is the probability to find the quantum system in $(x, \sigma, \bar{x}, \bar{\sigma})$ at time t . In the absence of magnetic fields, the wave function depends on the spin coordinates only parametrically since the Hamiltonian does not depend on the spin coordinates. To simplify the notation we therefore suppress the spin coordinates in the sequel although we include the dependence on the spin in Pauli exclusion principle for the electron wave functions. We assume the atomic units (a.u.) in which the mass and charge of the electron are equal to one, and the Planck constant is $\hbar = 1$. We denote by M_n the mass of individual nuclei.

The quantum mechanical evolution is described by the Schrödinger equation for a wave function $\Phi : \mathbb{R}^{3N} \times \mathbb{R}^{3J} \times [0, \infty) \rightarrow \mathbb{C}$ satisfying

$$i \partial_t \Phi(x, \bar{x}, t) = \hat{\mathcal{H}} \Phi(x, \bar{x}, t), \tag{2.1}$$

with the Hamiltonian operator

$$\hat{\mathcal{H}} = - \sum_{n=1}^N \frac{1}{2M_n} \Delta_{x^n} + \hat{W}(x, \bar{x}) + V_b(x) + v_b(x, \bar{x}), \tag{2.2}$$

where $V_b : \mathbb{R}^{3N} \rightarrow \mathbb{R}$ and $v_b : \mathbb{R}^{3N} \times \mathbb{R}^{3J} \rightarrow \mathbb{R}$ are given ad hoc external scalar smooth potentials and $\hat{W}(x, \bar{x})$ is the electronic operator formed by the electron kinetic energy,

electron-electron repulsion, nuclei-nuclei repulsion and electron-nuclei attraction, see [2, 9, 10],

$$\begin{aligned} \hat{W}(x, \bar{x}) &= -\frac{1}{2}\Delta_{\bar{x}} + \nu(x, \bar{x}) \\ \nu(x, \bar{x}) &= \sum_{j=1}^J \sum_{k < j} \frac{1}{|\bar{x}^k - \bar{x}^j|} + \sum_{m=1}^N \sum_{n < m} \frac{Z_n Z_m}{|x^n - x^m|} - \sum_{j=1}^J \sum_{n=1}^N \frac{Z_n}{|x^n - \bar{x}^j|}. \end{aligned} \tag{2.3}$$

Here Z_n denotes the charge of the n th nucleus and $\bar{x}^j \in \mathbb{R}^3$ the coordinate of the electron j . The external potentials $V_b: \mathbb{R}^{3N} \rightarrow \mathbb{R}$ and $v_b: \mathbb{R}^{3N} \times \mathbb{R}^{3J} \rightarrow \mathbb{R}$ make the system confined and do not perturb the system far away from the boundary by the assumptions

$$\begin{aligned} v_b(x, \bar{x}) &:= \sum_{j=1}^J h(|\bar{x}^j - x^0|), \\ h(y) &\rightarrow \infty \quad \text{as } y \rightarrow \infty, \\ h(y) &= 0 \quad \text{for } |y| \leq C, \\ V_b(x) &\rightarrow \infty \quad \text{as } |x| \rightarrow \infty, \\ V_b(x) &= 0 \quad \text{for } |x| \leq C, \end{aligned} \tag{2.4}$$

with a large constant C , where $x^0 := \sum_{n=1}^N x^n / N$ and $h: \mathbb{R} \rightarrow \mathbb{R}$ is a given smooth function.

2.2. The electronic operator. The electron eigenvalue problem takes the form

$$(\hat{W} + v_b)\Psi_k = \lambda_k \Psi_k, \tag{2.5}$$

with each function Ψ_k in the anti-symmetric wave function subspace of L^2 , based on \bar{x} and the electron spin coordinates. Since $\hat{W} + v_b$ depends on the nuclei coordinate x only parametrically, the eigenfunctions and eigenvalues will depend on x . We will see that the eigenvalues λ_k , $k = 1, \dots$ will be the potentials for the nuclei dynamics which determine the molecular dynamics. The work [4–6, 14] use the explicit pair interactions of their potentials to define the energy related to each particle and to treat the conservation of total momentum. Our ab initio potentials λ_k are not given by pair interactions. To derive the conservation laws from the quantum mechanical formulation (2.1), we will in particular use two properties of the electron eigenvalue problem (2.12), namely its invariance with respect to translations and rotations in \mathbb{R}^3 and its construction by pair interactions.

2.2.1. Rotational invariance. We note that $\hat{W} + v_b$ is invariant with respect to the affine transformations defined by

$$(x^1, \dots, x^N, \bar{x}^1, \dots, \bar{x}^J) \mapsto (Qx^1 + \alpha, \dots, Qx^N + \alpha, Q\bar{x}^1 + \alpha, \dots, Q\bar{x}^J + \alpha),$$

where $Q \in O(3)$ is an orthogonal transformation of \mathbb{R}^3 and $\alpha \in \mathbb{R}^3$ a translation, i.e.,

$$(\hat{W} + v_b)(x, \bar{x}) = (\hat{W} + v_b)(Qx^1 + \alpha, \dots, Qx^N + \alpha, Q\bar{x}^1 + \alpha, \dots, Q\bar{x}^J + \alpha).$$

Therefore also the eigenvalues λ_k and eigenfunctions are invariant with respect to such translations and orthogonal transformations.

2.2.2. Partition of the energy. Irving & Kirkwood and others [4, 5, 14, 15] used empirical pair potentials to determine the stress tensor and heat flux, based on a partition of the potential energy related to each particle. For pair interactions the potential energy takes the form

$$w(x) := \sum_n \sum_{m < n} \nu(|x_n - x_m|)$$

for some function $\nu : \mathbb{R} \rightarrow \mathbb{R}$ and the only natural splitting of the potential energy related to each particle n becomes

$$w^n(x) := \frac{1}{2} \sum_{m \neq n} \nu(|x_n - x_m|), \tag{2.6}$$

so that $w = \sum_n w^n$. This partition is unique in the sense that it splits each pair energy into two equal parts. In our case the potential energy, given by an electron eigenvalue, is not a pair potential. However, the corresponding operator for the electron problem is based on pair interactions and indistinguishable electrons, which we use to define a similar energy related to each particle: first, split in (2.7) the electron energy operator into a sum and then relate each term to the eigenvalues using eigenvalue perturbation theory as described below.

We now show how the summation over all particles in the definition of the potential operator (2.3) can be rearranged into a sum over contributions from each nucleus

$$\hat{W} = \sum_{n=1}^N \hat{W}^n. \tag{2.7}$$

For the ease of exposition we assume charge neutrality of the electron-nuclei system and we partition the electron index set $\mathcal{E} \equiv \{1, \dots, J\}$ into disjoint subsets \mathcal{E}_n , $n = 1, \dots, N$ such that $\bigcup_{n=1}^N \mathcal{E}_n = \mathcal{E}$ and the number of elements in \mathcal{E}_n is equal to Z_n , i.e., $\#\mathcal{E}_n = Z_n$, by letting

$$\mathcal{E}_1 = \{1, \dots, Z_1\}, \mathcal{E}_2 = \{Z_1 + 1, \dots, Z_1 + Z_2\}, \dots, \mathcal{E}_N = \{1 + \sum_{i=1}^{N-1} Z_i, \dots, \sum_{i=1}^N Z_i\}.$$

Using this partitioning we define

$$\hat{W}^n(x, \bar{x}) = -\frac{1}{2} \sum_{k \in \mathcal{E}_n} \Delta_{\bar{x}^k} + \frac{1}{2} \sum_{\ell \in \mathcal{E}_n} \sum_{k \neq \ell} \frac{1}{|\bar{x}^k - \bar{x}^\ell|} + \frac{1}{2} \sum_{m \neq n} \frac{Z_n Z_m}{|x^n - x^m|} - \sum_{k=1}^J \frac{Z_n}{|x^n - \bar{x}^k|}, \tag{2.8}$$

where the terms including the sums in \mathcal{E}_n correspond to the electron kinetic energy and electron-electron repulsion for electrons associated with the nucleus n . The partition (2.8) is unique, in the same sense as for (2.6), since it depends only on the numbering of the electron coordinates. We define the potential energy related to the nucleus n as

$$\lambda_k^n(x) = \left\langle \Psi_k(x), \left(\hat{W}^n + \frac{v_b}{N} \right) (x) \Psi_k(x) \right\rangle_e, \tag{2.9}$$

where we note that relabeling electron coordinates does not change the electron eigenvalue, due to the anti-symmetry condition. Therefore the ordering of the electron coordinates does not matter in (2.8). Here we denote by $\langle u, w \rangle_e = \sum_{\bar{\sigma} \in \bar{\Sigma}} \int_{\mathbb{R}^{3J}} u^*(\bar{x}, \bar{\sigma}) w(\bar{x}, \bar{\sigma}) d\bar{x}$

the scalar product on the Hilbert space $L^2(\mathbb{R}^{3J} \times \bar{\Sigma})$ of electron states. This definition can be motivated by standard perturbation analysis, see [8]: A small perturbation w of the potential $\hat{W} + v_b$ yields to leading order that the k th eigenvalue $\lambda_k = \langle \Psi_k, (\hat{W} + v_b) \Psi_k \rangle_e$ is perturbed to $\langle \Psi_k, (\hat{W} + v_b + w) \Psi_k \rangle_e$. The energy related to the particle n , for eigenvalue k , can therefore be viewed as the difference of λ_k and the k th eigenvalue for the perturbed potential $\hat{W} + v_b - (\hat{W}^n + v_b/N)$, which corresponds to removing particle n and its electrons and the fraction $1/N$ of the external potential v_b . This perturbed eigenvalue is, to the leading order,

$$\left\langle \Psi_k, (\hat{W} + v_b - (\hat{W}^n + v_b/N)) \Psi_k \right\rangle_e,$$

which leads to the definition in (2.9). Property (2.8) and (2.9) imply that for all k

$$\lambda_k = \sum_{n=1}^N \lambda_k^n. \tag{2.10}$$

In the introductory Section 3 we will consider only one energy surface, often the ground state $\lambda_1(x)$, and therefore we drop the index k there, and use the notation $\lambda := \lambda_k$ for a given fixed k . In Section 5 we use all electron eigenvalues λ_k , $k = 1, \dots, d$, to establish molecular dynamics representations of the stress tensor and the heat flux.

2.2.3. Reduction to finite dimensional electron space and regularization of the electron operator. To obtain the classical limits in Section 5 we first regularize the electron operator $\hat{W} + v_b$ by replacing all Coulomb terms $1/|z|$ in ν by $1/\sqrt{|z|^2 + \delta_a}$, with a positive constant $\delta_a > 0$. We note that this regularization preserves the translation and rotation invariance. Then we introduce a finite dimensional approximation V of $\hat{W} + v_b$ in the anti-symmetric electronic wave function space (including also the spin coordinates) by applying a projection onto the finite-dimensional subspace of $L^2(\mathbb{R}^{3J} \times \bar{\Sigma})$ spanned by the eigenfunctions $\{\Psi_1, \dots, \Psi_d\}$ of the regularized Hamiltonian $\hat{W} + v_b$, with the corresponding eigenvalues $\{\lambda_1, \dots, \lambda_d\}$, as

$$\begin{aligned} V\psi &= \sum_{k=1}^d \lambda_k \Psi_k \langle \Psi_k, \psi \rangle_e, \\ V^n \psi &= \sum_{k=1}^d \lambda_k^n \Psi_k \langle \Psi_k, \psi \rangle_e, \end{aligned} \tag{2.11}$$

for any wave function $\psi \in L^2(\mathbb{R}^{3J} \times \bar{\Sigma})$. Since we have $v_b(x, \bar{x}) \rightarrow \infty$ as $|\bar{x}| \rightarrow \infty$ for given x and the potential part in $\hat{W} + v_b$ is locally integrable with respect to \bar{x} , the spectrum of $\hat{W} + v_b$ is discrete, see [12].

The motivation to introduce the reduction (2.11) to a smooth $d \times d$ matrix with distinct eigenvalues is that we then have a precise result of the approximation of quantum observables by molecular dynamics, in particular Theorem 5.1 proved in [7]. Thus $\hat{W} + v_b$ is approximated by a Hermitian matrix-valued operator $V: \mathbb{R}^{3N} \rightarrow \mathbb{C}^{d \times d}$ by (2.11). We assume that the eigenvalues $\lambda_1(x), \lambda_2(x), \dots, \lambda_d(x)$ of this matrix-valued potential $V(x)$, i.e., solutions

$$V(x)\psi_k(x) = \lambda_k(x)\psi_k(x), \text{ for all } x \in \mathbb{R}^{3N}, \tag{2.12}$$

satisfy

$$\lambda_1(x) < \lambda_2(x) < \dots < \lambda_d(x), \tag{2.13}$$

$$\lambda_1(x) + V_b(x) \rightarrow \infty \text{ as } |x| \rightarrow \infty, \tag{2.14}$$

$$\lambda_d(x) \rightarrow \infty \text{ as } d \rightarrow \infty, \tag{2.15}$$

$$\{\lambda_k\}_{k=1}^d \text{ depend continuously on } \delta_a \text{ as } \delta_a \rightarrow 0+. \tag{2.16}$$

The first assumption is in order to have differentiable eigenvectors, the second condition implies that the system is confined, with respect to the nuclei, and the third condition is used to have a discrete spectrum of $\hat{W} + v_b$ and ensure that V is a consistent approximation of $\hat{W} + v_b$.

In general, nuclei positions x where electron eigenvalues coincide, e.g. points x where $\lambda_1(x) = \lambda_2(x)$, form a co-dimension two set in \mathbb{R}^{3N} . Such points include so-called conical intersections which are difficult to handle in the classical limit and they are not included in Theorem 5.1. Section 5.4 describes how an extension of Theorem 5.1 to include conical intersection could be possible.

2.3. The conservation laws. The conservation laws or balance laws for mass, momentum and energy, based on the density $\rho: \mathbb{R}^3 \times [0, \infty) \rightarrow [0, \infty)$, velocity $u: \mathbb{R}^3 \times [0, \infty) \rightarrow \mathbb{R}^3$ and energy density $E: \mathbb{R}^3 \times [0, \infty) \rightarrow \mathbb{R}$, take the form

$$\begin{aligned} \partial_t \rho(y, t) + \sum_{\ell=1}^3 \partial_{y_\ell} (\rho(y, t) u_\ell(y, t)) &= 0, \\ \partial_t (\rho(y, t) u_j(y, t)) + \sum_{\ell=1}^3 \partial_{y_\ell} (\rho(y, t) u_j(y, t) u_\ell(y, t) - \sigma_{\ell j}(y, t)) &= F_j(y, t), \\ \partial_t E(y, t) + \sum_{\ell=1}^3 \partial_{y_\ell} (E(y, t) u_\ell(y, t) + q_\ell(y, t) - \sum_{j=1}^3 \sigma_{\ell j}(y, t) u_j(y, t)) &= P(y, t), \end{aligned} \tag{2.17}$$

where $\sigma_{\ell j}: \mathbb{R}^3 \times [0, \infty) \rightarrow \mathbb{R}$ is the ℓj -component of the 3×3 stress tensor, $q_\ell: \mathbb{R}^3 \times [0, \infty) \rightarrow \mathbb{R}$ is the ℓ -th component of the heat flux, $F: \mathbb{R}^3 \times [0, \infty) \rightarrow \mathbb{R}^3$ is an external force and $P: \mathbb{R}^3 \times [0, \infty) \rightarrow \mathbb{R}$ is an external energy source. The purpose of this work is to derive these conservation/balance laws from microscopic dynamical systems. First we consider classical systems and then quantum systems.

3. The conservation laws derived from classical particle dynamics

In this section we consider a system of N classical particles, where each particle has mass M_n , position coordinate x^n and momentum coordinate p^n , $n = 1, \dots, N$. We use the notation $x = (x^1, x^2, x^3, \dots, x^N)$ and $p = (p^1, p^2, p^3, \dots, p^N)$. The position coordinates $x: [0, \infty) \rightarrow \mathbb{R}^{3N}$ and momentum coordinates $p: [0, \infty) \rightarrow \mathbb{R}^{3N}$ satisfy the classical equations of motion given by the Hamiltonian

$$H(x, p) = \sum_{n=1}^N \frac{1}{2M_n} |p^n|^2 + \lambda(x) + V_b(x), \tag{3.1}$$

where $\lambda: \mathbb{R}^{3N} \rightarrow \mathbb{R}$ is a given interaction potential which we relate to the potential energy surface, i.e. an eigenvalue $\lambda_k(x)$ in (2.12), in the next section and $V_b: \mathbb{R}^3 \rightarrow \mathbb{R}$ is the external potential. Thus the evolution of the system is given by the solution of Newtonian dynamics

$$\begin{aligned} \dot{x}_t^n &= \frac{1}{M_n} p_t^n, \quad n = 1, \dots, N \\ \dot{p}_t &= -\nabla \lambda(x_t) - \nabla V_b(x_t), \end{aligned}$$

where $x_t^n \in \mathbb{R}^3$ and $p_t^n \in \mathbb{R}^3$ is the position and momentum, respectively, of the particle n at time t . The given potential $\lambda: \mathbb{R}^{3N} \rightarrow \mathbb{R}$ is assumed to be invariant under the Euclidean group of transformations of \mathbb{R}^3 , i.e. $\lambda(x^1, \dots, x^N) = \lambda(Qx^1 + \alpha, \dots, Qx^N + \alpha)$ for any orthogonal 3×3 matrix Q and any translation $\alpha \in \mathbb{R}^3$. The following lemma will be used to represent the potential λ as a function of pairwise distances between particles rather than the positions of each particle. It shows that there is a transformation in the Euclidean group, which consists of isometries, that maps all elements of one point set to another point set, provided the distances between points in both sets coincide.

LEMMA 3.1. *If the two sets of points $\{x^i\}_{i=1}^N$ and $\{y^i\}_{i=1}^N$, where $x^i, y^i \in \mathbb{R}^3$, satisfy $r^{ij} = |x^i - x^j| = |y^i - y^j|$ for $1 \leq i, j \leq N$, then there exist an orthogonal matrix $Q \in \mathbb{R}^{3 \times 3}$ and a translation vector $\alpha \in \mathbb{R}^3$ such that $x^i = Qy^i + \alpha$ for $1 \leq i \leq N$.*

Proof. Let $\bar{x}^i := x^i - x^1, \bar{y}^i = y^i - y^1$, for $1 \leq i \leq N$. If $\bar{x}^i = \bar{y}^i = 0$, for all $1 \leq i \leq N$, then clearly the claim in the theorem is true. If not, let i_1 be an index such that $\bar{x}^{i_1} \neq 0$ (which also implies that $\bar{y}^{i_1} \neq 0$). Let $Q_1, Q_2 \in \mathbb{R}^{3 \times 3}$ be two orthogonal matrices such that $Q_1 \bar{x}^{i_1}$ and $Q_2 \bar{y}^{i_1}$ both lie on the first positive coordinate axis. Then clearly $Q_1 \bar{x}^{i_1} = Q_2 \bar{y}^{i_1}$.

Define $\bar{\bar{x}}^i := Q_1 \bar{x}^i$ and $\bar{\bar{y}}^i := Q_2 \bar{y}^i$ for all $1 \leq i \leq N$. If all $\bar{\bar{x}}^i$ and $\bar{\bar{y}}^i$ lie on the first coordinate axis then $\bar{\bar{x}}^i = \bar{\bar{y}}^i$, for $1 \leq i \leq N$, since every $\bar{\bar{x}}^i$ and $\bar{\bar{y}}^i$ have the same distance to $\bar{\bar{x}}^1$ in the origin, and $\bar{\bar{x}}^{i_1}$. Assume now that there exists an index i_2 such that $\bar{\bar{x}}^{i_2}$ does not lie on the first coordinate axis. Since $\bar{\bar{x}}^{i_2}$ and $\bar{\bar{y}}^{i_2}$ have the same distance to $\bar{\bar{x}}^1$ and $\bar{\bar{x}}^{i_1}$, also $\bar{\bar{y}}^{i_2}$ does not lie on the first coordinate axis. Let $Q_3, Q_4 \in \mathbb{R}^{3 \times 3}$ be two orthogonal matrices that are rotations around the first coordinate axis such that $Q_3 \bar{\bar{x}}^{i_2}$ and $Q_4 \bar{\bar{y}}^{i_2}$ are both in the “positive xy -plane”, i.e. given as $(a, b, 0)$ for $b > 0$. This makes $Q_3 \bar{\bar{x}}^{i_2} = Q_4 \bar{\bar{y}}^{i_2}$ since the points are on the same distance to $\bar{\bar{x}}^1$ and $\bar{\bar{x}}^{i_1}$.

Define $\bar{\bar{\bar{x}}}^i := Q_3 \bar{\bar{x}}^i$ and $\bar{\bar{\bar{y}}}^i := Q_4 \bar{\bar{y}}^i$ for all $1 \leq i \leq N$. Since the points $\bar{\bar{\bar{x}}}^i$ and $\bar{\bar{\bar{y}}}^i$ have the same distance to the points $\bar{\bar{x}}^1, \bar{\bar{x}}^{i_1}$, and $\bar{\bar{x}}^{i_2}$, that all lie in the plane spanned by the first two coordinate directions, but not all of them on a straight line, we must either have that $\bar{\bar{\bar{x}}}^i = \bar{\bar{\bar{y}}}^i$ or $\bar{\bar{\bar{x}}}^i = Q \bar{\bar{\bar{y}}}^i$, for the reflection in the xy -plane $Q = \begin{pmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{pmatrix}$. There cannot be two points $\bar{\bar{\bar{x}}}^i$ and $\bar{\bar{\bar{x}}}^j$ that do not lie in the xy -plane and satisfy $\bar{\bar{\bar{x}}}^i = \bar{\bar{\bar{y}}}^i$ and $\bar{\bar{\bar{x}}}^j = Q \bar{\bar{\bar{y}}}^j$, since then $\bar{\bar{\bar{x}}}^j$ and $\bar{\bar{\bar{y}}}^j$ would be on different distance from $\bar{\bar{x}}^1 = \bar{\bar{\bar{y}}}^1$.

Hence either $\bar{\bar{\bar{x}}}^i = \bar{\bar{\bar{y}}}^i$ for all $1 \leq i \leq N$, or $\bar{\bar{\bar{x}}}^i = Q \bar{\bar{\bar{y}}}^i$ for all $1 \leq i \leq N$. Since $\bar{\bar{x}}^i$ are obtained from x^i by the same set of translations and multiplications by orthogonal matrices for all $1 \leq i \leq N$, and likewise for $\bar{\bar{y}}^i$, the proof is complete. \square

To handle conservation of total momentum we will use Newton’s third law for pair interactions and we follow the construction in [1] to determine pair interactions in a general potential that is invariant with respect to translations and orthogonal transformations in \mathbb{R}^3 : knowing all $N(N-1)/2$ pair distances $r := (r^{12}, r^{13}, \dots, r^{N-1N}) := (|x^1 - x^2|, |x^1 - x^3|, \dots, |x^{N-1} - x^N|)$ determines x up to a translation and orthogonal transformation in \mathbb{R}^3 and since $\lambda(x)$ remains the same for such translations and orthogonal transformations the potential is determined by all pair distances, i.e.

$$\lambda(x) =: \tilde{\lambda}(r(x)). \tag{3.2}$$

We will use the partial derivatives $\partial_{r^{jk}} \tilde{\lambda}(r^{12}, r^{13}, \dots, r^{N-1N})$. Not all $r \in \mathbb{R}^{N(N-1)/2}$ correspond to particle positions $x \in \mathbb{R}^{3N}$ and there are $N(N-1)/2$ partial derivatives $\partial_{r^{jk}} \tilde{\lambda}(r)$ while the gradient $\nabla \lambda(x)$ only has $3N$ components. Therefore the partial derivatives $\partial_{r^{jk}} \tilde{\lambda}(r)$ are not uniquely defined by $\nabla \lambda(x)$. Section 7 shows how to determine $\partial_{r^{jk}} \tilde{\lambda}(r)$.

To define the observables for density, momentum and energy and their dependence on the space coordinate $y \in \mathbb{R}^3$ we use a non-negative smooth mollifier $\eta: \mathbb{R}^3 \rightarrow \mathbb{R}$, $\eta \in C^\infty(\mathbb{R}^3)$, with a compact support, satisfying

$$\begin{aligned} \int_{\mathbb{R}^3} \eta(y) dy &= 1, \\ \eta(y) &\geq 0, \quad \eta(y) = \eta(-y), \quad \text{for all } y \in \mathbb{R}^3, \\ \eta(y) &= 0, \quad \text{for } |y| > \epsilon. \end{aligned}$$

The macroscopic density $\rho: \mathbb{R}^3 \times [0, \infty) \rightarrow \mathbb{R}$ is defined by the particle system as

$$\rho(y, t) = \int_{\mathbb{R}^{6N}} \sum_n M_n \eta(y - x_t^n) f(x_0, p_0) dx_0 dp_0,$$

where x_t^n is a function of the initial condition (x_0, p_0) , and $f: \mathbb{R}^{6N} \rightarrow [0, \infty)$ is a given initial particle distribution function normalized so that $\int_{\mathbb{R}^{6N}} f(x_0, p_0) dx_0 dp_0 = 1$. Irving and Kirkwood, [5], use this definition with η equal to a point mass and a general initial distribution f . Noll, [14], formulates the integration with respect to point masses in terms of the one-point and two-point density correlations functions instead and provides precise conditions for the validity of the derivation. Hardy, [4], uses the mollifier η but not the integration over the initial particle distribution.

3.1. The conservation of mass. Let $z_0 = (x_0, p_0)$ denote the phase-space coordinate in \mathbb{R}^{6N} and $x \cdot y = \sum_{i=1}^3 x^i y^i$ the Euclidean scalar product in \mathbb{R}^3 . Differentiation of the density implies

$$\begin{aligned} \partial_t \rho(y, t) &= - \int_{\mathbb{R}^{6N}} \sum_{n=1}^N M_n \dot{x}_t^n \cdot \nabla \eta(y - x_t^n) f(z_0) dz_0 \\ &= - \int_{\mathbb{R}^{6N}} \sum_{n=1}^N p_t^n \cdot \nabla \eta(y - x_t^n) f(z_0) dz_0 \end{aligned} \tag{3.3}$$

and by defining the velocity $u: \mathbb{R}^3 \times [0, \infty) \rightarrow \mathbb{R}^3$ as

$$\rho(y, t) u(y, t) := \int_{\mathbb{R}^{6N}} \sum_{n=1}^N \eta(y - x_t^n) p_t^n f(z_0) dz_0 \tag{3.4}$$

we obtain the conservation law for the mass

$$\partial_t \rho(y, t) + \sum_{k=1}^3 \partial_{y_k} (\rho(y, t) u_k(y, t)) = 0.$$

3.2. The conservation of momentum. Differentiation of the momentum yields

$$\begin{aligned} \partial_t (\rho(y, t) u(y, t)) &= - \int_{\mathbb{R}^{6N}} \sum_{n=1}^N M_n^{-1} p_t^n \cdot \nabla \eta(y - x_t^n) p_t^n f(z_0) dz_0 \\ &\quad - \int_{\mathbb{R}^{6N}} \sum_{n=1}^N \eta(y - x_t^n) \nabla_{x^n} \lambda(x_t) f(z_0) dz_0 \\ &\quad - \int_{\mathbb{R}^{6N}} \sum_{n=1}^N \eta(y - x_t^n) \nabla_{x^n} V_b(x_t) f(z_0) dz_0. \end{aligned}$$

In order to write the second term as a divergence term we follow Noll's, [14], and Hardy's method, [4], based on identifying gradients with respect to pair distances and converting the difference in η at the corresponding point to a gradient term: the combination of the pair distance derivative, using the definition of $\tilde{\lambda}$ in (3.2),

$$\begin{aligned} \sum_{n=1}^N \eta(y-x^n) \nabla_{x^n} \lambda &= \sum_n \sum_{j < k} \eta(y-x^n) \partial_{r^{jk}} \tilde{\lambda}(r) \nabla_{x^n} (|x^j-x^k|) \\ &= \sum_{n < k} (\eta(y-x^n) - \eta(y-x^k)) \partial_{r^{nk}} \tilde{\lambda}(r) \nabla_{x^n} (|x^n-x^k|) \end{aligned} \tag{3.5}$$

and the difference at the corresponding points

$$\begin{aligned} \eta(y-x^n) - \eta(y-x^k) &= \int_0^1 \frac{d}{ds} \eta(y-sx^n - (1-s)x^k) ds \\ &= \int_0^1 (x^k-x^n) \cdot \nabla \eta(y-sx^n - (1-s)x^k) ds \\ &= -\operatorname{div}_y \int_0^1 \eta(y-sx^n - (1-s)x^k) (x^n-x^k) ds \end{aligned} \tag{3.6}$$

shows that

$$\begin{aligned} \sum_n \eta(y-x^n) \nabla_{x^n} \lambda &= -\operatorname{div}_y \left(\sum_{n < k} \int_0^1 \eta(y-sx^n - (1-s)x^k) (x^n-x^k) ds \right) \\ &\quad \times \partial_{r^{nk}} \tilde{\lambda}(r) \nabla_{x^n} |x^n-x^k|. \end{aligned}$$

We conclude that the following conservation law for the momentum holds

$$\begin{aligned} \partial_t (\rho(y,t) u_j(y,t)) &= - \sum_{\ell=1}^3 \partial_{y_\ell} \int_{\mathbb{R}^{6N}} \sum_{n=1}^N M_n^{-1} \eta(y-x_t^n) p_j^n(t) p_\ell^n(t) f(z_0) dz_0 \\ &\quad + \sum_{\ell=1}^3 \partial_{y_\ell} \int_{\mathbb{R}^{6N}} \sum_{n < k} \int_0^1 \eta(y-sx_t^n - (1-s)x_t^k) (x_\ell^n(t) - x_\ell^k(t)) ds \\ &\quad \quad \times \partial_{r^{nk}} \tilde{\lambda} \partial_{x_t^n} (|x_t^n - x_t^k|) f(z_0) dz_0. \\ &\quad - \int_{\mathbb{R}^{6N}} \sum_{n=1}^N \eta(y-x_t^n) \nabla_{x^n} V_b(x_t) f(z_0) dz_0. \end{aligned} \tag{3.7}$$

To write the conservation law for momentum in the form (2.17) we follow the steps in [14]. Let

$$v_t^n := \frac{p_t^n}{M_n} - u(y,t)$$

where by (3.4)

$$u(y,t) = \frac{\int_{\mathbb{R}^{6N}} \sum_{n=1}^N \eta(y-x_t^n) p_t^n f(z_0) dz_0}{\int_{\mathbb{R}^{6N}} \sum_{n=1}^N M_n \eta(y-x_t^n) f(z_0) dz_0}.$$

Definition (3.4) implies

$$\int_{\mathbb{R}^{6N}} \sum_{n=1}^N M_n \eta(y - x_t^n) v_t^n f(z_0) dz_0 = 0$$

so that the first integral in (3.7) satisfies

$$\begin{aligned} & \int_{\mathbb{R}^{6N}} \sum_{n=1}^N M_n^{-1} \eta(y - x_t^n) p_j^n(t) p_\ell^n(t) f(z_0) dz_0 \\ &= \int_{\mathbb{R}^{6N}} \sum_{n=1}^N M_n \eta(y - x_t^n) (v_j^n(t) v_\ell^n(t) + u_j(t) v_\ell^n(t) + v_j^n(t) u_\ell(t) + u_j(t) u_\ell(t)) f(z_0) dz_0 \\ &= \int_{\mathbb{R}^{6N}} \sum_{n=1}^N M_n \eta(y - x_t^n) (v_j^n(t) v_\ell^n(t) + u_j(t) u_\ell(t)) f(z_0) dz_0. \end{aligned}$$

The conservation law for the momentum can therefore be formulated as

$$\partial_t(\rho(y, t) u_j(y, t)) + \sum_{\ell=1}^3 \partial_{y_\ell}(\rho(y, t) u_j(y, t) u_\ell(y, t) - \sigma_{\ell j}(y, t)) = F_j(y, t),$$

where

$$\begin{aligned} \sigma_{\ell j}(y, t) &:= \int_{\mathbb{R}^{6N}} \tilde{\sigma}_{\ell j}(x_t, p_t; y, t) f(x_0, p_0) dx_0 dp_0, \\ \tilde{\sigma}_{\ell j}(x, p; y, t) &:= - \sum_{n=1}^N M_n \eta(y - x^n) v_j^n v_\ell^n \\ &\quad + \sum_{n < k} \int_0^1 \eta(y - s x^n - (1-s)x^k) (x_\ell^n - x_\ell^k) ds \\ &\quad \times \partial_{r, n k} \tilde{\lambda} \partial_{x_j^n} (|x^n - x^k|), \end{aligned} \tag{3.8}$$

defines the stress tensor using $v^n = M_n^{-1} p^n - u(y, t)$, and

$$F(y, t) := - \int_{\mathbb{R}^{6N}} \sum_{n=1}^N \eta(y - x_t^n) \nabla_{x^n} V_b(x_t) f(z_0) dz_0 \tag{3.9}$$

defines the macroscopic external force.

3.3. The conservation of energy. In order to define the energy density we need to define the potential energy related to each particle. In the case of pair potentials this is straight forward by summing the pair potentials including the particle, as in [4, 5, 14]. Since we have a more general potential, which does not have to be a sum of pair potentials, this step requires a new construction: here we use the potential energy λ^n , related to the particle n , introduced in (2.9) and (2.10).

We define the energy density $E: \mathbb{R}^3 \times [0, \infty) \rightarrow \mathbb{R}$ by

$$E(y, t) = \int_{\mathbb{R}^{6N}} \sum_n \eta(y - x_t^n) \left(\frac{|p_t^n|^2}{2M_n} + \lambda^n(x_t) \right) f(x_0, p_0) dx_0 dp_0$$

and differentiate it to obtain

$$\begin{aligned} \partial_t E_t(y, t) &= - \int_{\mathbb{R}^{6N}} \sum_n M_n^{-1} p_t^n \cdot \nabla \eta(y - x_t^n) \left(\frac{|p^n|^2}{2M_n} + \lambda^n(x_t) \right) f(x_0, p_0) dx_0 dp_0 \\ &\quad - \int_{\mathbb{R}^{6N}} \sum_n M_n^{-1} \eta(y - x_t^n) p_t^n \cdot \nabla_{x^n} (\lambda(x_t) + V_b(x_t)) f(x_0, p_0) dx_0 dp_0 \\ &\quad + \int_{\mathbb{R}^{6N}} \sum_{n,m} M_m^{-1} \eta(y - x_t^n) p_t^m \cdot \nabla_{x^m} \lambda^n(x_t) f(x_0, p_0) dx_0 dp_0. \end{aligned} \tag{3.10}$$

We have

$$\begin{aligned} \sum_n M_n^{-1} \eta(y - x_t^n) p_t^n \cdot \nabla_{x^n} \lambda(x_t) &= \sum_{n,m} M_n^{-1} \eta(y - x_t^n) p_t^n \cdot \nabla_{x^n} \lambda^m(x_t) \\ &= \sum_{n,m} M_m^{-1} \eta(y - x_t^m) p_t^m \cdot \nabla_{x^m} \lambda^n(x_t), \end{aligned}$$

so the right-hand side in (3.10) becomes

$$\begin{aligned} \partial_t E(y, t) &= - \sum_{\ell=1}^3 \partial_{y_\ell} \int_{\mathbb{R}^{6N}} \sum_n M_n^{-1} p_\ell^n(t) \eta(y - x_t^n) \left(\frac{|p^n|^2}{2M_n} + \lambda^n(x_t) \right) f(x_0, p_0) dx_0 dp_0 \\ &\quad + \int_{\mathbb{R}^{6N}} \sum_{n,m} (\eta(y - x_t^n) - \eta(y - x_t^m)) (M_m^{-1} p_t^m) \cdot \nabla_{x^m} \lambda^n(x_t) f(x_0, p_0) dx_0 dp_0 \\ &\quad - \int_{\mathbb{R}^{6N}} \sum_n M_n^{-1} \eta(y - x_t^n) p_t^n \cdot \nabla_{x^n} V_b(x_t) f(x_0, p_0) dx_0 dp_0. \end{aligned}$$

By using (3.6) we obtain the conservation law for the energy

$$\begin{aligned} &\partial_t E(y, t) \\ &= - \sum_{\ell=1}^3 \partial_{y_\ell} \int_{\mathbb{R}^{6N}} \sum_n M_n^{-1} p_\ell^n(t) \eta(y - x_t^n) \left(\frac{|p^n|^2}{2M_n} + \lambda^n(x_t) \right) f(x_0, p_0) dx_0 dp_0 \\ &\quad - \sum_{\ell=1}^3 \partial_{y_\ell} \int_{\mathbb{R}^{6N}} \sum_{n,m} \int_0^1 \eta(y - x_t^m + s(x_t^m - x_t^n)) ds (x_\ell^n(t) - x_\ell^m(t)) \\ &\quad \quad \times (M_m^{-1} p_t^m) \cdot \nabla_{x^m} \lambda^n(x_t) f(x_0, p_0) dx_0 dp_0 \\ &\quad - \int_{\mathbb{R}^{6N}} \sum_n M_n^{-1} \eta(y - x_t^n) p_t^n \cdot \nabla_{x^n} V_b(x_t) f(x_0, p_0) dx_0 dp_0. \end{aligned} \tag{3.11}$$

In order to write the energy conservation in the standard form (2.17) we use

$$\begin{aligned} &\sum_{n=1}^N \eta(y - x^n) (u_\ell + v_\ell^n) \left(\frac{|p^n|^2}{2M_n} + \lambda^n(x) \right) \\ &= \sum_{n=1}^N \eta(y - x^n) u_\ell \left(\frac{|p^n|^2}{2M_n} + \lambda^n(x) \right) + \sum_{n=1}^N \eta(y - x^n) v_\ell^n \left(\frac{M_n |v^n|^2}{2} + \lambda^n(x) \right) \\ &\quad + \sum_{n=1}^N \eta(y - x^n) M_n v_\ell^n \frac{|u|^2}{2} + \sum_{n=1}^N \eta(y - x^n) M_n v_\ell^n u \cdot v^n. \end{aligned}$$

The first term in the right-hand side becomes $E(y,t)u_\ell(y,t)$ under the integration in (3.11), and the last term is part of $\sum_j \sigma_{\ell j}(y,t)u_j(y,t)$. The term including the factor $v_\ell^n |u|^2$ vanishes upon integration over the initial distribution due to the definition (3.4) and the second term is included in the heat flux. The conservation of energy can therefore be written

$$\partial_t E(y,t) + \sum_{\ell=1}^3 \partial_{y_\ell} (E(y,t)u_\ell(y,t) + q_\ell(y,t) - \sum_j \sigma_{\ell j}(y,t)u_j(y,t)) = P(y,t)$$

where the heat flux is defined as

$$\begin{aligned} q_\ell(y,t) &:= \int_{\mathbb{R}^{6N}} \tilde{q}_\ell(x_t, p_t; y, t) f(x_0, p_0) dx_0 dp_0, \\ \tilde{q}_\ell(x, p; y, t) &:= \sum_n v_\ell^n \eta(y - x^n) \left(\frac{M_n |v^n|^2}{2} + \lambda^n(x) \right) \\ &\quad + \sum_{n,m} \int_0^1 \eta(y - x^m + s(x^m - x^n)) ds (x_\ell^n - x_\ell^m) \times \\ &\quad \times \left(\frac{p^m}{M_m} \cdot \nabla_{x^m} \lambda^n(x) - \sum_j u_j(y,t) \partial_{r^{nm}} \lambda(x(r^{12}, \dots, r^{N-1N})) \partial_{x_j^n} |x^n - x^m| \right), \end{aligned} \tag{3.12}$$

and the external energy source as

$$P(y,t) := - \int_{\mathbb{R}^{6N}} \sum_n M_n^{-1} \eta(y - x_t^n) p_t^n \cdot \nabla_{x^n} V_b(x_t) f(x_0, p_0) dx_0 dp_0. \tag{3.13}$$

4. The conservation laws derived from quantum mechanics

Irving and Zwanzig [6] derived the conservation laws when the particle system is modeled by the Schrödinger equation for a wave function $\Phi: \mathbb{R}^{3(N+J)} \times [0, \infty) \rightarrow \mathbb{C}$ satisfying

$$i \partial_t \Phi(\tilde{x}, t) = \hat{H} \Phi(\tilde{x}, t), \tag{4.1}$$

with the Hamiltonian

$$\hat{H} = - \sum_{n=1}^{N+J} \frac{1}{2\tilde{M}_n} \Delta_{\tilde{x}^n} + \nu(\tilde{x}),$$

based on the nuclei and electron coordinates now written together as $\tilde{x} = (x, \bar{x}) \in \mathbb{R}^{3(N+J)}$ with particle masses of nuclei and electrons denoted by $\tilde{M}_n = M_n, n = 1, \dots, N$, and $\tilde{M}_n = 1, n = N + 1, \dots, N + J$, as defined in (2.3). The wave function Φ is in an appropriate subset of $L^2(\mathbb{R}^{3(N+J)})$ taking anti-symmetry of electron coordinates into account. Irving and Zwanzig used the Wigner function to establish correspondence between classical and quantum observables.

We use instead the related Weyl quantization, which associates to a (Weyl) symbol $A: \mathbb{R}^{6(N+J)} \rightarrow \mathbb{C}$, i.e., a classical observable $A(x, \bar{x}, p, \bar{p})$, an operator on $L^2(\mathbb{R}^{3(J+N)})$, in fact the Weyl quantization represents an isomorphism between $L^2(\mathbb{R}^{3(J+N)})$ and the space of Hilbert-Schmidt operators on $L^2(\mathbb{R}^{3(J+N)})$. The Weyl quantized operator \hat{A}

associated with the symbol A in the Schwartz space acting on a function $\phi \in L^2(\mathbb{R}^{3(J+N)})$ is defined by

$$\hat{A}\phi(\tilde{x}) = \left(\frac{1}{2\pi}\right)^{3(N+J)} \int_{\mathbb{R}^{6(N+J)}} e^{i(\tilde{x}-\tilde{x}')\cdot\tilde{p}} A\left(\frac{1}{2}(\tilde{x}+\tilde{x}'), \tilde{p}\right) \phi(\tilde{x}') d\tilde{x}' d\tilde{p}, \tag{4.2}$$

and the definition is extended to more general symbols A by the standard density arguments. For instance, quantization of the Hamiltonian symbol

$$H(\tilde{x}, \tilde{p}) = \sum_{n=1}^{N+J} \frac{|\tilde{p}_n|^2}{2\tilde{M}_n} + \nu(\tilde{x})$$

yields the operator \hat{H} .

We recall that the dependence on spin variables is only parametric and it does not enter the quantization procedure since we consider observables and Hamiltonians that do not depend on spin operators, for example modelling systems in absence of magnetic fields, or spin orbit coupling interactions etc. Therefore we omit spin variables $\sigma, \bar{\sigma}$ in the notation. However, we note that the scalar product of wave functions $\phi, \psi \in L^2(\mathbb{R}^{3(J+N)} \times \Sigma \times \bar{\Sigma})$ is $\langle \phi, \psi \rangle = \sum_{\sigma} \sum_{\bar{\sigma}} \int_{L^2(\mathbb{R}^{3(J+N)})} \phi^*(x, \sigma, \bar{\sigma}) \psi(x, \sigma, \bar{\sigma}) dx d\bar{x}$.

The Schrödinger equation implies the evolution of the wave function $\Phi(\cdot, t) = e^{-it\hat{H}}\Phi(\cdot, 0)$ and consequently an observable at time t defined by $\langle \Phi(\cdot, t), \hat{A}\Phi(\cdot, t) \rangle$ satisfies

$$\langle \Phi(\cdot, t), \hat{A}\Phi(\cdot, t) \rangle = \langle \Phi(\cdot, 0), e^{it\hat{H}} \hat{A} e^{-it\hat{H}} \Phi(\cdot, 0) \rangle.$$

By defining the evolution of observables as

$$\hat{A}_t := e^{it\hat{H}} \hat{A} e^{-it\hat{H}} \tag{4.3}$$

differentiation implies the Heisenberg-von Neumann equation

$$\partial_t \hat{A}_t = i[\hat{H}, \hat{A}_t],$$

where $[\hat{B}, \hat{C}] = \hat{B}\hat{C} - \hat{C}\hat{B}$ is the commutator. We also obtain

$$\partial_t \hat{A}_t = ie^{it\hat{H}} [\hat{H}, \hat{A}] e^{-it\hat{H}} \tag{4.4}$$

and $\hat{A}_0 = \hat{A}$. Let \hat{f} be the Weyl quantization of any initial classical density distribution $f: \mathbb{R}^{6(N+J)} \rightarrow \mathbb{R}$. Section 6 presents a precise definition of a density symbol related to the given initial data of the macroscopic density, momentum and energy. The Irving and Zwanzig quantum density observable is then defined by the $L^2(\mathbb{R}^{3(J+N)} \times \Sigma \times \bar{\Sigma})$ trace

$$\begin{aligned} \rho(y, t) &= \text{Tr}(\hat{\rho}_t \hat{f}) \\ &:= \sum_{j=1}^{\infty} \langle \Phi_j, \hat{\rho}_t \hat{f} \Phi_j \rangle \end{aligned} \tag{4.5}$$

where $\{\Phi_j\}_{j=1}^{\infty}$ is a basis of the subspace of $L^2(\mathbb{R}^{3(N+J)} \times \Sigma \times \bar{\Sigma})$ based on the symmetry conditions of fermions and bosons and the density observable is the quantization of the density symbol

$$\hat{\rho}_0 = \left(\sum_{n=1}^{N+J} \tilde{M}_n \eta(y - \tilde{x}^n) \right) \hat{}$$

The quantum momentum and energy observables are analogously defined as

$$\begin{aligned} \hat{p}_0 &= \left(\sum_{n=1}^{N+J} \eta(y - \tilde{x}^n) \tilde{p}^n \right)^\wedge, \\ \hat{E}_0 &= \left(\sum_{n=1}^{N+J} \eta(y - \tilde{x}^n) \left(\frac{|\tilde{p}^n|^2}{2M_n} + \nu^n(\tilde{x}) \right) \right)^\wedge, \end{aligned} \tag{4.6}$$

where $\nu = \sum_{n=1}^{N+J} \nu^n$ is a partition with the potential energy related to each particle, analogous to (2.8), now defined as

$$\nu^n(x, \tilde{x}) = \begin{cases} \frac{1}{2} \sum_{m \neq n} \frac{Z_n Z_m}{|x^n - x^m|} - \sum_{k=1}^J \frac{Z_n}{|x^n - \tilde{x}^k|} & \text{for } n \leq N \\ \frac{1}{2} \sum_{\ell \neq n} \frac{1}{|\tilde{x}^n - \tilde{x}^\ell|} & \text{for } n \geq N + 1. \end{cases}$$

Irving and Zwanzig observed the following crucial property.

LEMMA 4.1. *For any twice differentiable scalar symbol that is a polynomial of degree two in the momentum variable*

$$A(\tilde{x}, \tilde{p}) := a_0(\tilde{x}) + \sum_{n=1}^{N+J} a_n(\tilde{x}) \cdot \tilde{p}^n + \sum_{m,n=1}^{N+J} a_{n,m}(\tilde{x}) \tilde{p}^n \cdot \tilde{p}^m \in \mathbb{C} \tag{4.7}$$

there holds

$$\begin{aligned} i[\hat{H}, \hat{A}] &= \left(\nabla_{\tilde{p}} H(\tilde{x}, \tilde{p}) \cdot \nabla_{\tilde{x}} A(\tilde{x}, \tilde{p}) - \nabla_{\tilde{x}} H(\tilde{x}, \tilde{p}) \cdot \nabla_{\tilde{p}} A(\tilde{x}, \tilde{p}) \right)^\wedge \\ &=: \{H(\tilde{x}, \tilde{p}), A(\tilde{x}, \tilde{p})\}^\wedge, \end{aligned}$$

where $a_0(\tilde{x}) \in \mathbb{R}, a_n(\tilde{x}) \in \mathbb{R}^3, a_{n,m}(\tilde{x}) \in \mathbb{R}^{3 \times 3}$.

The result is also known in the mathematics literature, cf. [11, Remarks 2.6.9 and 2.7.6], and we include a proof of the lemma in Section 4.1, since it is important for this work. The lemma shows that for a symbol that is a polynomial of degree at most two in the momentum variable the quantum evolution of the observable reduces to the classical evolution based on the Poisson bracket. The quantum observables for density, momentum and energy are based precisely on symbols which are degree zero, one and two, respectively, in the momentum variable. Irving and Zwanzig therefore conclude that the quantum observables satisfy analogous conservation laws as those for classical particle dynamics, namely: differentiation of the density and using (4.4), Lemma 4.1, and the definition of \hat{p} imply the conservation of mass

$$\begin{aligned} \partial_t \rho(y, t) &= \text{Tr} \left(\partial_t \hat{\rho}_t \hat{f} \right) \\ &= \text{Tr} \left(e^{it\hat{H}} i[\hat{H}, \hat{\rho}_0] e^{-it\hat{H}} \hat{f} \right) \\ &= \text{Tr} \left(e^{it\hat{H}} \{H, \rho_0\}^\wedge e^{-it\hat{H}} \hat{f} \right) \\ &= -\text{Tr} \left(e^{it\hat{H}} \text{div}_y \hat{p}_0 e^{-it\hat{H}} \hat{f} \right) \\ &= -\text{div} \left(\text{Tr} \left(\hat{p}_t \hat{f} \right) \right), \end{aligned} \tag{4.8}$$

where the first equality follows by the definition of the macroscopic density (4.5), the second by the Heisenberg-von Neumann dynamics of quantum observables (4.4), the

third by Lemma 4.1, the fourth by $\{H, \rho_0\} = -\sum_n \nabla \eta(y - x^n) p^n = -\operatorname{div}_y p_0$ using (4.6) and the fifth by the definition of quantum time evolution (4.3).

Similarly differentiation of the momentum and energy establish the conservation laws for the momentum

$$\begin{aligned} \partial_t \operatorname{Tr}(\hat{p}_t \hat{f}) &= -\sum_{\ell=1}^3 \partial_{y_\ell} \operatorname{Tr} \left(\left(\sum_{n=1}^N \tilde{M}_n^{-1} \eta(y - \tilde{x}^n) \tilde{p}^n \tilde{p}_\ell^n \right. \right. \\ &\quad \left. \left. + \sum_n \sum_m \int_0^1 \eta(y - s\tilde{x}^n - (1-s)\tilde{x}^m) (\tilde{x}_\ell^n - \tilde{x}_\ell^m) ds \right. \right. \\ &\quad \left. \left. \times \partial_{r^{nm}} \nu(\tilde{x}(r^{12}, \dots, r^{N+J-1N+J})) \nabla_{\tilde{x}^n} |\tilde{x}^n - \tilde{x}^m| \right)_t \hat{f} \right) \end{aligned} \quad (4.9)$$

and the energy

$$\begin{aligned} \partial_t \operatorname{Tr}(\hat{E}_t \hat{f}) &= -\sum_{\ell=1}^3 \partial_{y_\ell} \operatorname{Tr} \left(\left(\sum_n \tilde{M}_n^{-1} \tilde{p}_\ell^n \eta(y - \tilde{x}^n) \left(\frac{|\tilde{p}^n|^2}{2\tilde{M}_n} + \nu^n(\tilde{x}) \right) \right. \right. \\ &\quad \left. \left. + \sum_{n,m} \int_0^1 \eta(y - \tilde{x}^m + s(\tilde{x}^m - \tilde{x}^n)) ds (\tilde{x}_\ell^n - \tilde{x}_\ell^m) (\tilde{M}_m^{-1} \tilde{p}^m) \cdot \nabla_{\tilde{x}^m} \nu^n(\tilde{x}) \right)_t \hat{f} \right). \end{aligned} \quad (4.10)$$

4.1. Proof of Lemma 4.1. We have the composition rule $\hat{B}\hat{C} = \hat{D}$ where

$$D = e^{\frac{i}{2}(\nabla_{\tilde{x}'} \cdot \nabla_{\tilde{p}} - \nabla_{\tilde{x}} \cdot \nabla_{\tilde{p}'})} B(\tilde{x}, \tilde{p}) C(\tilde{x}', \tilde{p}') \Big|_{\substack{\tilde{x} = \tilde{x}' \\ \tilde{p} = \tilde{p}'}} =: B \# C, \quad (4.11)$$

see [20, Theorem 4.11]. Therefore

$$[\hat{H}, \hat{A}] = (H \# A)^\wedge - (A \# H)^\wedge$$

and, letting \tilde{M} denote the diagonal matrix with \tilde{M}_n in the diagonal, we obtain

$$\begin{aligned} &(\nabla_{\tilde{x}} \cdot \nabla_{\tilde{p}'} - \nabla_{\tilde{x}'} \cdot \nabla_{\tilde{p}})(H(\tilde{x}, \tilde{p})A(\tilde{x}', \tilde{p}') - A(\tilde{x}, \tilde{p})H(\tilde{x}', \tilde{p}')) \\ &= \nabla \nu(\tilde{x}) \cdot \nabla_{\tilde{p}} A(\tilde{x}', \tilde{p}') - \tilde{M}^{-1} \tilde{p} \cdot \nabla_{\tilde{x}} A(\tilde{x}', \tilde{p}') \\ &\quad - \nabla_{\tilde{x}} A(\tilde{x}, \tilde{p}) \cdot \tilde{M}^{-1} \tilde{p}' + \nabla \nu(\tilde{x}') \cdot \nabla_{\tilde{p}} A(\tilde{x}, \tilde{p}) \\ &= \nabla \nu(\tilde{x}) \cdot \nabla_{\tilde{p}} A(\tilde{x}', \tilde{p}') + \nabla \nu(\tilde{x}') \cdot \nabla_{\tilde{p}} A(\tilde{x}, \tilde{p}) \\ &\quad - \tilde{M}^{-1} \tilde{p} \cdot \nabla_{\tilde{x}} A(\tilde{x}', \tilde{p}') - \tilde{M}^{-1} \tilde{p}' \cdot \nabla_{\tilde{x}} A(\tilde{x}, \tilde{p}) =: \text{I}(\tilde{x}, \tilde{x}', \tilde{p}, \tilde{p}'). \end{aligned}$$

Evaluation at the point $(\tilde{x}', \tilde{p}') = (\tilde{x}, \tilde{p})$ yields

$$\frac{i^2}{2} (\nabla_{\tilde{x}'} \cdot \nabla_{\tilde{p}} - \nabla_{\tilde{x}} \cdot \nabla_{\tilde{p}'}) (H(\tilde{x}, \tilde{p})A(\tilde{x}', \tilde{p}') - A(\tilde{x}, \tilde{p})H(\tilde{x}', \tilde{p}')) \Big|_{\substack{\tilde{x} = \tilde{x}' \\ \tilde{p} = \tilde{p}'}} = \{H, A\}.$$

The differentiation to the second order becomes

$$\begin{aligned} (\nabla_{\tilde{x}} \cdot \nabla_{\tilde{p}'} - \nabla_{\tilde{x}'} \cdot \nabla_{\tilde{p}}) I(\tilde{x}, \tilde{x}', \tilde{p}, \tilde{p}') &= \sum_{m,n} \partial_{\tilde{x}^m} \partial_{\tilde{x}^n} \nu(\tilde{x}) \partial_{\tilde{p}^m} \partial_{\tilde{p}^n} A(\tilde{x}', \tilde{p}') \\ &\quad - \sum_{m,n} \partial_{\tilde{x}^m} \partial_{\tilde{x}^n} \nu(\tilde{x}') \partial_{\tilde{p}^m} \partial_{\tilde{p}^n} A(\tilde{x}, \tilde{p}) \\ &\quad - \sum_n \tilde{M}_n^{-1} \partial_{\tilde{x}^n}^2 A(\tilde{x}, \tilde{p}) \\ &\quad + \sum_n \tilde{M}_n^{-1} \partial_{\tilde{x}^n}^2 A(\tilde{x}', \tilde{p}') =: \text{II}(\tilde{x}, \tilde{x}', \tilde{p}, \tilde{p}'), \end{aligned}$$

so that $\Pi(\tilde{x}, \tilde{x}, \tilde{p}, \tilde{p}) = 0$.

Since the symbol A is a polynomial of degree two in the momentum variable we have

$$(\nabla_{\tilde{x}} \cdot \nabla_{\tilde{p}'} - \nabla_{\tilde{x}'} \cdot \nabla_{\tilde{p}})\Pi(\tilde{x}, \tilde{x}', \tilde{p}, \tilde{p}') = 0$$

which together with the Taylor expansion of the exponential proves the lemma.

4.2. Regularization of the observables. The use of the semiclassical analysis in the next section requires conditions on the observables, which are not satisfied for $\eta(y - x^n)$. Therefore we replace in the proof of Theorem 5.2 the function $\eta(y - x^n)$ by

$$\eta_{\delta_p}(y, x^n, p^n) := \eta(y - x^n)\zeta(|p^n|^2) \tag{4.12}$$

where $\zeta : \mathbb{R} \rightarrow [0, \infty)$ is a smooth cut-off function satisfying

$$\zeta(q) = \begin{cases} 1 & \text{for } |q| < 1/\delta_p, \\ 0 & \text{for } |q| > 2/\delta_p, \end{cases}$$

for a small positive constant $\delta_p > 0$.

5. The classical limit of the quantum conservation laws

This section first extends the formulation of quantum conservation laws to the case with matrix-valued potentials in Subsection 5.1, and then in Subsection 5.2 this formulation is used to derive molecular dynamics limits of the stress tensor and the heat flux consistent with the quantum conservation laws as formulated in Theorem 5.2. Therefore we will redefine the notation for the Hamiltonian H and rescale the Weyl quantization $A \mapsto \hat{A}$ and the composition operator $\#$.

5.1. Quantum conservation laws with matrix-valued potentials. The aim here is to consider the quantum evolution where the electron part is considered matrix valued and the Weyl quantization is only in the nuclei part. For simplicity all nuclei masses are assumed to be equal, $M_n = M$, and we assume that the nuclei electron mass ratio $M \gg 1$ is large. The case with individual masses is treated by a change of variables in Section 5.3. To obtain the classical molecular dynamics limit, as $M \rightarrow \infty$, we restrict the electron operator to the finite dimensional $d \times d$ matrix V in (2.12). We also change the time scale so that the nuclei dynamics has a limit, when $M \rightarrow \infty$, as follows: the wave function related to (4.1) can be written as $\Phi : \mathbb{R}^{3N} \times [0, \infty) \rightarrow \mathbb{C}^d$ and it solves the Schrödinger equation

$$\frac{i}{M^{1/2}} \partial_\tau \Phi(x, \tau) = \hat{H} \Phi(x, \tau),$$

with the change of the time scale $\tau = M^{-1/2}t$. The classical limit obtained as $M \rightarrow \infty$ is well behaved in this time scale, in the sense that the nuclei move a distance of order one in time one, as we shall see in Theorem 5.1. The Hamiltonian is now defined as

$$\hat{H} = -\frac{1}{2M} \Delta_x \mathbf{I} + V(x) + V_b(x) \mathbf{I}$$

with the Hermitian $d \times d$ matrix V defined in (2.11), the external potential V_b satisfying (2.4) and \mathbf{I} the $d \times d$ identity matrix. In this time scale the corresponding Heisenberg-von Neumann equation takes the form

$$\partial_\tau \hat{A}_\tau = iM^{1/2} [\hat{H}, \hat{A}_\tau]$$

for the $d \times d$ matrix-valued symbol $A_\tau(x, p)$. This form of matrix-valued symbols are suitable for studying the $M \rightarrow \infty$ limit of the observables we have in the conservation laws, since the corresponding Weyl quantizations are based on highly oscillatory Fourier integral operators that only use the nuclei coordinates. We also assume that the eigenvalues $\lambda_1(x), \lambda_2(x), \dots, \lambda_d(x)$ of $V(x)$, defined by (2.12), satisfy (2.13)-(2.16). The new Weyl quantization takes the form

$$\hat{A}\phi(x) = \left(\frac{M^{1/2}}{2\pi}\right)^{3N} \int_{\mathbb{R}^{3N}} \int_{\mathbb{R}^{3N}} e^{iM^{1/2}(x-y)\cdot p} A\left(\frac{1}{2}(x+y), p\right)\phi(y) dp dy,$$

which differs from (4.2) by the scaling $M^{1/2}$. Although this form of matrix-valued symbols H and A is useful to obtain the classical limit as $M \rightarrow \infty$, matrix-valued symbols introduce a complication: the important property in Lemma 4.1 that the commutator with respect to the conservation observables reduces to the quantization of the Poisson bracket does not hold for matrix-valued symbols, since these matrices do not commute in general, unless the symbols are diagonal. The main tool to determine the classical limit is therefore to diagonalize H and the observables A_τ in the conservation laws, based on the composition operator $\#$, as follows.

The symbol C for the product of two Weyl operators $\hat{A}\hat{B} = \hat{C}$ is determined by

$$C(z, p) = e^{\frac{i}{2M^{1/2}}(\nabla_{z'} \cdot \nabla_p - \nabla_z \cdot \nabla_{p'})} A(z, p)B(z', p') \Big|_{\substack{z=z' \\ p=p'}} =: (A\#B)(z, p), \tag{5.1}$$

see [20, Theorem 4.11] which now includes the scaling $M^{1/2}$ as compared to (4.11). Let $\Psi: \mathbb{R}^{3N} \rightarrow \mathbb{C}^{d^2}$ satisfy that $\Psi(x)$ is a unitary matrix for every x with the Hermitian transpose $\Psi^*(x)$, and define $\bar{A}: \mathbb{R}^{3N} \times [0, \infty) \rightarrow \mathbb{C}^{d^2}$ by

$$\hat{A}_\tau = \Psi(x)\hat{A}_\tau\Psi^*(x)$$

so that

$$\hat{A}_\tau = \Psi^*(x)\hat{A}_\tau\Psi(x).$$

Then

$$[\hat{H}, \hat{A}_\tau] = \Psi[\Psi^*\hat{H}\Psi, \hat{A}_\tau]\Psi^*$$

and consequently

$$\partial_\tau \hat{A}_\tau = iM^{1/2}[\Psi^*\hat{H}\Psi, \hat{A}_\tau].$$

The composition rule (5.1) yields $\Psi^*\hat{H}\Psi = (\Psi^*\#H\#\Psi)^\wedge$. The next step is to determine Ψ so that

$$\bar{\bar{H}} := \Psi^*\#H\#\Psi$$

is diagonal or approximate diagonal. Having $\bar{\bar{H}}$ diagonal implies that $\hat{\hat{H}}$ is diagonal and then \hat{A} remains diagonal if it is initially diagonal, since then

$$\partial_\tau \hat{A}_{jk}(\tau) = iM^{1/2}(\hat{\hat{H}}_{jj}\hat{A}_{jk}(\tau) - \hat{A}_{jk}(\tau)\hat{\hat{H}}_{kk}) = 0, \quad \text{for } j \neq k.$$

The composition rule (5.1) with

$$H(x,p) = \left(\frac{|p|^2}{2} + V_b(x)\right)I + V(x)$$

implies that

$$\begin{aligned} \bar{H} &= \Psi^* \# H \# \Psi \\ &= \left(\frac{|p|^2}{2} + V_b(x)\right)I + \Psi^* V \Psi + \frac{1}{4M} \nabla \Psi^* \cdot \nabla \Psi \\ &= \Psi^* \left(\left(\frac{|p|^2}{2} + V_b(x)\right)I + V + \frac{1}{4M} \nabla \Psi \nabla \Psi^* \cdot \nabla \Psi \Psi^* \right) \Psi, \end{aligned}$$

as verified in [7, Lemma 3.1]. Therefore the aim is to choose the unitary matrix Ψ so that it is an approximate solution to the nonlinear eigenvalue problem

$$\left(V + \frac{1}{4M} \nabla \Psi \nabla \Psi^* \cdot \nabla \Psi \Psi^*\right) \Psi = \Psi \bar{\Lambda} \tag{5.2}$$

where $\bar{\Lambda}$ is diagonal. A solution, Ψ , to this nonlinear eigenvalue problem is an $\mathcal{O}(M^{-1})$ perturbation of the eigenvectors to $V(x)$ provided the eigenvalues do not cross and M is sufficiently large. The work [7, (3.18)] shows that under the same assumptions as Theorem 5.1, Equation (5.2) has an approximate solution Ψ that satisfies

$$\left(V + \frac{1}{4M} \nabla \Psi \nabla \Psi^* \cdot \nabla \Psi \Psi^*\right) \Psi = \Psi \bar{\Lambda} + \mathcal{O}(M^{-2}), \tag{5.3}$$

with $\bar{\Lambda}$ diagonal, based on the following iteration. Let $\Psi_0 = [\psi_1 \ \psi_2 \ \dots \ \psi_d]$ be the matrix of eigenvectors to V . The approximate eigenvectors Ψ are the normalized eigenvectors of

$$V + \frac{1}{4M} \Psi_0 \nabla \Psi_0^* \cdot \nabla \Psi_0 \Psi_0^*$$

and $\bar{\Lambda}$ are the corresponding eigenvalues. Since regular perturbation theory shows $\|\Psi - \Psi_0\|_{C^1(\mathbb{R}^{3N})} = \mathcal{O}(M^{-1})$ we obtain

$$\bar{H}(x,p) = \bar{H}(x,p) + r_0(x)$$

where the remainder $d \times d$ matrix $r_0(x)$ is small

$$\|r_0\|_{L^\infty(\mathbb{R}^N)} = \mathcal{O}(M^{-2}), \tag{5.4}$$

with the diagonal matrix

$$\bar{H}(x,p) := \left(\frac{|p|^2}{2} + V_b(x)\right)I + \bar{\Lambda}(x). \tag{5.5}$$

We also need a partition of the eigenvalues $\bar{\Lambda} = \sum_{n=1}^N \bar{\Lambda}^n$ related to the potential energy for each particle similar to (2.9), now including also the small nonlinear part. In fact, the nonlinear part also has a natural composition into particle contributions, now based on the sensitivity of the eigenvectors with respect to position x^n . With V^n defined by (2.11) we have

$$V + \frac{1}{4M} \nabla \Psi \nabla \Psi^* \cdot \nabla \Psi \Psi^* = \sum_{n=1}^N \left(V^n + \frac{1}{4M} \nabla \Psi \nabla_{x^n} \Psi^* \cdot \nabla_{x^n} \Psi \Psi^* \right)$$

and define for $n = 1, \dots, N$

$$\begin{aligned} \bar{\lambda}_k^n &:= \langle \Psi_k, (V^n + \frac{1}{4M} \Psi \nabla_{x^n} \Psi^* \cdot \nabla_{x^n} \Psi \Psi^*) \Psi_k \rangle, k = 1, \dots, d, \\ \bar{\Lambda}^n &= \text{diag}(\bar{\lambda}_1^n, \dots, \bar{\lambda}_d^n), \end{aligned} \tag{5.6}$$

which implies

$$\begin{aligned} \bar{\lambda}_k &= \sum_{n=1}^N \bar{\lambda}_k^n, \\ \bar{\Lambda} &= \sum_{n=1}^N \bar{\Lambda}_k^n. \end{aligned}$$

We will use the observables defining density, momentum and energy as follows. Let

$$\bar{\rho}_0(x, y) = \sum_{n=1}^N \eta(y - x^n) \mathbf{I}$$

and as before its time evolution is determined by the Heisenberg-von Neumann equation

$$\partial_\tau \hat{\rho}_\tau = iM^{1/2} [\hat{H}, \hat{\rho}_\tau],$$

with the solution

$$\hat{\rho}_\tau = e^{i\tau M^{1/2} \hat{H}} \hat{\rho}_0 e^{-i\tau M^{1/2} \hat{H}},$$

which shows that the time evolution can also be written as

$$\partial_\tau \hat{\rho}_\tau = iM^{1/2} e^{i\tau M^{1/2} \hat{H}} [\hat{H}, \hat{\rho}_0] e^{-i\tau M^{1/2} \hat{H}}. \tag{5.7}$$

The momentum and energy density symbols are defined as

$$\begin{aligned} \bar{p}_0 &= \sum_{n=1}^N \eta(y - x^n) p^n \mathbf{I}, \\ \bar{E}_0 &= \sum_{n=1}^N \eta(y - x^n) \left(\frac{|p^n|^2}{2} \mathbf{I} + \bar{\Lambda}^n(x) \right). \end{aligned}$$

The next step is to derive the quantum conservation/balance laws by studying the evaluation of the observables for density, momentum and energy. Let $\hat{f} = \Psi \bar{f} \Psi^*$ be the Weyl quantization of a given density symbol $\bar{f}(x, p) \in \mathbb{R}^{d \times d}$ as described precisely in Section 6.

LEMMA 5.1. *Assume that the eigenvalues $\lambda_k, k = 1, \dots, d$ of V are distinct and there are positive constants C and c such that*

$$\begin{aligned} \sum_{|\alpha| \leq 2} \|\partial^\alpha \psi_k\|_{L^2(\mathbb{R}^{3N})} + \sum_{|\alpha| \leq 2} \|\partial^\alpha \lambda_k\|_{L^2(\mathbb{R}^{3N})} + \|\bar{f}\|_{L^2(\mathbb{R}^{6N})} + \|\bar{\rho}_0\|_{L^2(\mathbb{R}^{6N})} &\leq C, \\ \|\bar{f}\|_{L^1(\mathbb{R}^{6N})} &> c, \end{aligned}$$

then

$$\begin{aligned} \partial_\tau \text{Tr}(\Psi \hat{\rho}_\tau \Psi^* \hat{f}) &= \partial_\tau \text{Tr}(\hat{\rho}_\tau \hat{f}), \\ \partial_\tau \text{Tr}(\hat{\rho}_\tau \hat{f}) &= -\text{div}(\text{Tr}(\hat{p}_\tau \hat{f})) + \mathcal{O}(M^{-3/2}) \text{Tr}(\hat{f}), \end{aligned} \tag{5.8}$$

as $M \rightarrow \infty$.

As compared to (4.8), the quantum continuity Equation (5.8) includes a $\mathcal{O}(M^{-3/2})$ remainder term, due to non-perfect diagonalization in (5.3).

Proof. We have

$$[\hat{H}, \hat{\rho}_0] = [\hat{H}, \bar{\rho}_0] + [\hat{r}_0, \hat{\rho}_0],$$

where $\|r_0\|_{L^\infty(\mathbb{R}^{3N})} = \mathcal{O}(M^{-2})$ by (5.4).

The diagonal form of \hat{H} combined with the property that the symbols $\bar{\rho}_0, \bar{p}_0, \bar{E}_0$ and \bar{H} are polynomials of degree at most two as functions of the momentum coordinate imply by Lemma 4.1, rewritten in the new scaling, the reduction of the corresponding quantum commutators to classical Poisson brackets. In the new scaling Lemma 4.1 takes the form: assume that \bar{H} and \bar{A} are diagonal matrices where each component of \bar{A} is a polynomial of degree at most two in p , as in (4.7), then $iM^{1/2}[\hat{H}, \hat{A}] = \{\bar{H}, \bar{A}\}^\wedge$. Therefore, we have as in (4.8)

$$iM^{1/2}[\hat{H}, \hat{\rho}_0] = \{\bar{H}, \bar{\rho}_0\}^\wedge = -\text{div}_y \hat{p}_0,$$

and by (5.7)

$$\partial_\tau \hat{\rho}_\tau = -\text{div}_y \hat{p}_\tau + iM^{1/2} e^{i\tau M^{1/2} \hat{H}} [\hat{r}_0, \hat{\rho}_0] e^{-i\tau M^{1/2} \hat{H}}. \tag{5.9}$$

By taking the trace in (5.9) the conservation law for the mass becomes

$$\begin{aligned} \partial_\tau \text{Tr}(\Psi \hat{\rho}_\tau \Psi^* \hat{f}) &= \partial_\tau \text{Tr}(\hat{\rho}_\tau \Psi^* \hat{f} \Psi) \\ &= \partial_\tau \text{Tr}(\hat{\rho}_\tau \hat{f}) \\ &= -\text{div}(\text{Tr}(\hat{p}_\tau \hat{f})) + \text{Tr}(iM^{1/2} e^{i\tau M^{1/2} \hat{H}} [\hat{r}_0, \hat{\rho}_0] e^{-i\tau M^{1/2} \hat{H}} \hat{f}), \end{aligned} \tag{5.10}$$

The next step is to estimate the remainder term including r_0 . Cauchy's inequality in the Hilbert-Schmidt inner product $\text{Tr}(\hat{A}^* \hat{B})$ implies that the remainder term has the estimate

$$\begin{aligned} &|\text{Tr}(iM^{1/2} e^{i\tau M^{1/2} \hat{H}} [\hat{r}_0, \hat{\rho}_0] e^{-i\tau M^{1/2} \hat{H}} \hat{f})| \\ &\leq M^{1/2} \left(\text{Tr}([\hat{r}_0, \hat{\rho}_0]^2) \text{Tr}((e^{-i\tau M^{1/2} \hat{H}} \hat{f} e^{i\tau M^{1/2} \hat{H}})^* e^{-i\tau M^{1/2} \hat{H}} \hat{f} e^{i\tau M^{1/2} \hat{H}}) \right)^{1/2} \\ &= M^{1/2} (\text{Tr}([\hat{r}_0, \hat{\rho}_0]^2) \text{Tr}(\hat{f}^* \hat{f}))^{1/2} \\ &= M^{1/2} \left(\text{Tr}((r_0 \# \bar{\rho}_0 - \bar{\rho}_0 \# r_0)^\wedge)^2 \right) \text{Tr}(\hat{f}^* \hat{f})^{1/2}. \end{aligned} \tag{5.11}$$

The Weyl quantization satisfies

$$\begin{aligned} \text{Tr}(\hat{A}) &= \left(\frac{\sqrt{M}}{2\pi} \right)^{3N} \int_{\mathbb{R}^{6N}} \text{Tr}(A(z)) dz, \\ \text{Tr}(\hat{A}\hat{B}) &= \left(\frac{\sqrt{M}}{2\pi} \right)^{3N} \int_{\mathbb{R}^{6N}} \text{Tr}(A(z)B(z)) dz, \end{aligned}$$

where $A(z)B(z)$ is the matrix product of the two $d \times d$ matrices $A(z)$ and $B(z)$, with the second trace acting on matrices, see [16] and [7, Lemma 3.1]. This isometry between Hilbert-Schmidt operators and $L^2(\mathbb{R}^{6N}, \mathbb{C}^{d \times d})$ functions also extends the Weyl quantization from symbols in the Schwartz class to $L^2(\mathbb{R}^{6N}, \mathbb{C}^{d \times d})$, see [16]. Lemma 5.2 implies

$$\begin{aligned} \text{Tr} \left(((r_0 \# \bar{\rho}_0 - \bar{\rho}_0 \# r_0)^\wedge)^2 \right) &= \left(\frac{\sqrt{M}}{2\pi} \right)^{3N} \int_{\mathbb{R}^{6N}} \text{Tr} \left((r_0 \# \bar{\rho}_0 - \bar{\rho}_0 \# r_0)^2 \right) dz \\ &\leq 4 \left(\frac{\sqrt{M}}{2\pi} \right)^{3N} \|r_0\|_{L^\infty(\mathbb{R}^{3N})}^2 \|\bar{\rho}_0\|_{L^2(\mathbb{R}^{6N})}^2 \end{aligned}$$

and we obtain by (5.4) and (5.11)

$$|\text{Tr} (iM^{1/2} e^{i\tau M^{1/2} \hat{H}} [\hat{r}_0, \hat{\rho}_0] e^{-i\tau M^{1/2} \hat{H}} \hat{f})| = \mathcal{O}(M^{-3/2}) \text{Tr}(\hat{f}),$$

which by (5.10) and (5.11) proves the lemma. □

The work [7, Lemma 3.11] proves

LEMMA 5.2. *Assume $D: \mathbb{R}^{6N} \rightarrow \mathbb{C}^{d \times d}$ belong to $L^2(\mathbb{R}^{6N})$ and $A: \mathbb{R}^{3N} \rightarrow \mathbb{C}^{d \times d}$ depends only on the x -coordinate (or only on the p -coordinate) and is bounded in $L^\infty(\mathbb{R}^{3N})$ then*

$$\begin{aligned} \|A \# D\|_{L^2(\mathbb{R}^{6N})} &\leq \|A\|_{L^\infty(\mathbb{R}^{3N})} \|D\|_{L^2(\mathbb{R}^{6N})}, \\ \|D \# A\|_{L^2(\mathbb{R}^{6N})} &\leq \|A\|_{L^\infty(\mathbb{R}^{3N})} \|D\|_{L^2(\mathbb{R}^{6N})}. \end{aligned} \tag{5.12}$$

The conservation of momentum and energy are also based on the reduction from commutators to Poisson brackets, in Lemma 4.1, as follows

$$\begin{aligned} \partial_\tau \hat{p}_\tau &= -\text{div} \left(\sum_n \eta(y - x^n) p^n \otimes p^n \mathbf{I} \right)_\tau \\ &\quad - \text{div} \left(\sum_n \sum_k \int_0^1 \eta(y - sx^n - (1-s)x^k) (x_\ell^n - x_\ell^k) ds \right. \\ &\quad \left. \times \partial_{r^{nk}} \bar{\Lambda}^n(x(r^{12}, \dots, r^{N-1N})) \nabla_{x^n} |x^n - x^k| \right)_\tau \\ &\quad - \underbrace{\left(\sum_n \eta(y - x^n) \nabla_{x^n} V_b(x) \right)_\tau}_{=:-\hat{F}(x,y)} + \underbrace{iM^{1/2} e^{i\tau M^{1/2} \hat{H}} [\hat{r}_0, \hat{\rho}_0] e^{-i\tau M^{1/2} \hat{H}}}_{=:R_1} \\ &:= -\text{div} \hat{S}_\tau + \hat{F}_\tau + R_1, \\ \partial_\tau \hat{E}_\tau &= -\text{div} \left(\sum_n \eta(y - x^n) p^n \left(\frac{|p^n|^2}{2} \mathbf{I} + \bar{\Lambda}^n(x) \right) \right)_\tau \\ &\quad - \text{div} \left(\sum_n \int_0^1 \eta(y - x^m + s(x^m - x^n)) ds (x^n - x^m) p^m \cdot \nabla_{x^m} \bar{\Lambda}^n \right)_\tau \\ &\quad - \underbrace{\left(\sum_n M_n^{-1} \eta(y - x^n) p^n \cdot \nabla_{x^n} V_b(x) \right)_\tau}_{=:-\hat{P}(x,y)} + \underbrace{iM^{1/2} e^{i\tau M^{1/2} \hat{H}} [\hat{r}_0, \hat{E}_0] e^{-i\tau M^{1/2} \hat{H}}}_{=:R_2} \end{aligned}$$

$$=: -\operatorname{div}\hat{Q}_\tau + \hat{P}_\tau + R_2. \tag{5.13}$$

As for the conservation of mass in Lemma 5.1 we obtain the conservation/balance law for the momentum

$$\partial_\tau \operatorname{Tr}(\Psi \hat{p}_\tau \Psi^* \hat{f}) = -\operatorname{div}(\operatorname{Tr}(\Psi \hat{S}_\tau \Psi^* \hat{f})) + \operatorname{Tr}(\Psi \hat{F}_\tau \Psi^* \hat{f}) + \mathcal{O}(M^{-3/2})\operatorname{Tr}(\hat{f}), \tag{5.14}$$

and the conservation/balance law for the energy

$$\partial_\tau \operatorname{Tr}(\hat{\Psi} \hat{E}_\tau \hat{\Psi}^* \hat{f}) = -\operatorname{div}(\operatorname{Tr}(\hat{\Psi} \hat{Q}_\tau \hat{\Psi}^* \hat{f})) + \operatorname{Tr}(\hat{\Psi} \hat{P}_\tau \hat{\Psi}^* \hat{f}) + \mathcal{O}(M^{-3/2})\operatorname{Tr}(\hat{f}), \tag{5.15}$$

provided $\bar{p}_0, \bar{S}_0, \bar{F}_0, \bar{E}_0, \bar{Q}_0, \bar{P}_0$ are all bounded in $L^2(\mathbb{R}^{6N})$.

In Section 6 we will motivate an initial density $\hat{f} = \hat{\Psi} \hat{f} \hat{\Psi}^*$ as a local grand canonical Gibbs density, where \hat{f} is diagonal, with the local temperature and chemical potential determined by the macroscopic density and energy. That is, \hat{f} is diagonalized by the same transformation as \hat{H} . The traces in the quantum conservation laws (5.8), (5.14) and (5.15) can then be written as

$$\operatorname{Tr}(\Psi \hat{A}_\tau \Psi^* \hat{f}) = \operatorname{Tr}(\hat{A}_\tau \hat{f}) = \operatorname{Tr}(\hat{A}_\tau \Psi^* \hat{f} \Psi) = \operatorname{Tr}(\hat{A}_\tau \hat{f})$$

where \bar{A} is diagonal and equal to $\bar{\rho}, \bar{p}, \bar{E}, \bar{S}$ and \bar{Q} , respectively. The next section presents the classical limit of these traces.

5.2. The molecular dynamics limit of the quantum conservation laws.

The work [7] proves in Theorem 3.7 the following, which provides the classical limit of the quantum observables in the conservation laws. A related result, with different assumptions, is in [16]. The proof is based on Weyl’s law, see [7, 16] namely that quantum observables have the classical representation

$$\frac{\operatorname{Tr}(\hat{A}_0 \hat{f})}{\operatorname{Tr}(\hat{f})} = \frac{\sum_{j=1}^d \int_{\mathbb{R}^{6N}} \bar{A}_{jj}(0, z) \bar{f}_{jj}(z) dz}{\sum_{j=1}^d \int_{\mathbb{R}^{6N}} \bar{f}_{jj}(z) dz} \tag{5.16}$$

for any $\bar{A}_{jj}(0, \cdot) \in L^2(\mathbb{R}^{6N})$ and $\bar{f}_{jj} \in L^2(\mathbb{R}^{6N}) \cap L^1(\mathbb{R}^{6N})$.

THEOREM 5.1. *Assume that V satisfies the coercivity condition (2.14), the $d \times d$ matrices \bar{A}_0 and \bar{f} are diagonal, the $d \times d$ matrix-valued Hamiltonian H has distinct eigenvalues, and that there is a constant C such that*

$$\sum |\alpha| \leq 2 \|\partial_x^\alpha \psi_k\|_{L^\infty(\mathbb{R}^{3N})} \leq C, \quad k = 1, \dots, d,$$

$$\max_i \sum_{|\alpha| \leq 3} \|\partial_x^\alpha \partial_{x_i} \lambda_j\|_{L^\infty(\mathbb{R}^{3N})} \leq C,$$

$$\sum |\alpha| \leq 3 \|\partial_z^\alpha \bar{A}_{jj}(0, \cdot)\|_{L^2(\mathbb{R}^{6N})} \leq C,$$

$$\|\bar{f}\|_{L^2(\mathbb{R}^{6N})} \leq C,$$

hold, then there is a constant c , depending on C , such that the canonical ensemble average satisfies the error estimate

$$\left| \frac{\operatorname{Tr}(\hat{A}_\tau \hat{f})}{\operatorname{Tr}(\hat{f})} - \sum_{j=1}^d \int_{\mathbb{R}^{6N}} \frac{\bar{A}_{jj}(0, z_\tau^j(z_0)) \bar{f}_{jj}(z_0)}{\sum_{k=1}^d \int_{\mathbb{R}^{6N}} \bar{f}_{kk}(z) dz} dz_0 \right| \leq cM^{-1},$$

as the mass ratio $M \rightarrow \infty$, where $z_\tau^j = (x_\tau, p_\tau)$ is the solution to the Hamiltonian system

$$\begin{aligned} \dot{x}_\tau &= p_\tau \\ \dot{p}_\tau &= -\nabla \bar{\lambda}_j(x_\tau) - \nabla V_b(x_\tau), \quad \tau > 0, \end{aligned} \tag{5.17}$$

based on the Hamiltonian $\bar{H}_{jj}(z) = |p|^2/2 + \bar{\lambda}_j(x) + V_b(x)$, with initial data $(x_0, p_0) = z_0$.

We note that the classical limit can be written

$$\sum_{j=1}^d \int_{\mathbb{R}^{6N}} \frac{\bar{A}_{jj}(0, z_\tau^j(z_0)) \bar{f}_{jj}(z_0)}{\sum_{k=1}^d \int_{\mathbb{R}^{6N}} \bar{f}_{kk}(z) dz} dz_0 = \sum_{j=1}^d \int_{\mathbb{R}^{6N}} q_j^* \bar{A}_{jj}(0, z_\tau^j(z_0)) \frac{\bar{f}_{jj}(z_0)}{\int_{\mathbb{R}^{6N}} \bar{f}_{jj}(z) dz} dz_0$$

where the probability, q_j^* , to be in electron state j is

$$q_j^* := \frac{\int_{\mathbb{R}^{6N}} \bar{f}_{jj}(z) dz}{\sum_{k=1}^d \int_{\mathbb{R}^{6N}} \bar{f}_{kk}(z) dz}, \quad j = 1, \dots, d. \tag{5.18}$$

To apply Theorem 5.1 to the quantum observables (5.8), (5.14) and (5.15) for macroscopic density, momentum and energy the momentum variable η needs to be regularized, since e.g. the momentum symbol $\bar{p}_0 = \sum_n \eta(y - x^n) p^n \mathbf{I}$ is not in $L^2(\mathbb{R}^{6N})$. Therefore we regularize all symbols by replacing $\eta(y - x^n)$ by $\eta_{\delta_p} := \eta(y - x^n) \zeta(|p^n|^2)$, given in (4.12), and denote the quantum observables using η_{δ_p} instead of η in (5.8), (5.14) and (5.15) as $\text{Tr}(\hat{\rho}_\tau \hat{f})_{\delta_p}$ (replacing $\text{Tr}(\hat{\rho}_\tau \hat{f})$ and similarly for the other observables).

ASSUMPTION 5.1. Assume that, for any regularization δ_a and dimension d , the quantum observables

$$\text{Tr}(\hat{\rho}_\tau \hat{f})_{\delta_p}, \text{Tr}(\hat{p}_\tau \hat{f})_{\delta_p}, \text{Tr}(\hat{S}_\tau \hat{f})_{\delta_p}, \text{Tr}(\hat{E}_\tau \hat{f})_{\delta_p}, \text{Tr}(\hat{Q}_\tau \hat{f})_{\delta_p}, \text{Tr}(\hat{P}_\tau \hat{f})_{\delta_p} \tag{5.19}$$

and their derivatives with respect to τ and y have limits as $\delta_p \rightarrow 0+$, with the limits based on $\eta = \eta_0$.

Theorem 5.1 and the assumed continuous dependence on the regularization parameters can be used to show a consistency result, namely that as the nuclei electron mass ratio M tends to infinity in the quantum conservation laws (5.8), (5.14) and (5.15), using the splitting $p_\tau^n = v_\tau^n + u(y, \tau)$ for the fluxes \bar{S} and \bar{Q} , we obtain the following limit in the form of a macroscopic conservation/balance law based on a certain stress tensor and heat flux defined by molecular dynamics including several electron eigenvalues. We note that the diagonal terms in the flux terms \bar{S} and \bar{Q} are the same as in the classical dynamics (3.7) and (3.11).

THEOREM 5.2. Assume that the approximate electron operator V satisfies (2.13)-(2.16) and Assumption 5.1 and the assumptions in Theorem 5.1 hold, with \bar{A} diagonal and equal to $\bar{\rho}_0, \bar{p}_0, \bar{E}_0, \bar{S}_0$ and \bar{Q}_0 , then as the nuclei-electron mass ratio $M \rightarrow \infty$ the quantum conservation laws (5.8), (5.14) and (5.15) have a classical molecular dynamics

limit that satisfies

$$\begin{aligned} \partial\tau\rho(y,t) + \sum_{\ell=1}^3 \partial_{y_\ell}(\rho(y,t)u_\ell(y,\tau)) &= 0, \\ \partial\tau(\rho(y,\tau)u_j(y,\tau)) + \sum_{\ell=1}^3 \partial_{y_\ell}(\rho(y,\tau)u_j(y,\tau)u_\ell(y,\tau) - \sigma_{\ell j}(y,\tau)) &= F_j(y,t), \\ \partial\tau E(y,\tau) + \sum_{\ell=1}^3 \partial_{y_\ell}(E(y,\tau)u_\ell(y,\tau) + q_\ell(y,\tau) - \sum_j \sigma_{\ell j}(y,\tau)u_j(y,\tau)) &= P(y,t), \end{aligned} \quad (5.20)$$

where

$$\begin{aligned} \rho(y,\tau) &= \sum_{j=1}^{\infty} q_j^* \int_{\mathbb{R}^{6N}} \bar{\rho}_{jj}(z_\tau^j, y) \bar{f}_{jj}(z_0) dz_0, \\ u(y,\tau) &= \sum_j q_j^* \int_{\mathbb{R}^{6N}} \bar{p}_{jj}(z_\tau^j, y) \bar{f}_{jj}(z_0) dz_0 / \rho(y,\tau), \\ E(y,\tau) &= \sum_j q_j^* \int_{\mathbb{R}^{6N}} \bar{E}_{jj}(z_\tau^j, y) \bar{f}_{jj}(z_0) dz_0, \\ \sigma(y,\tau) &= \sum_j q_j^* \int_{\mathbb{R}^{6N}} \bar{\sigma}(z_\tau^j; y, \tau) \bar{f}_{jj}(z_0) dz_0, \\ q(y,\tau) &= \sum_j q_j^* \int_{\mathbb{R}^{6N}} \bar{q}(z_\tau^j; y, \tau) \bar{f}_{jj}(z_0) dz_0, \\ F(y,\tau) &= \sum_j q_j^* \int_{\mathbb{R}^{6N}} \bar{F}(z_\tau^j, y, \tau) \bar{f}_{jj}(z_0) dz_0, \\ P(y,\tau) &= \sum_j q_j^* \int_{\mathbb{R}^{6N}} \bar{P}(z_\tau^j, y, \tau) \bar{f}_{jj}(z_0) dz_0, \\ q_j^* &= \frac{\int_{\mathbb{R}^{6N}} \bar{f}_{jj}(z) dz}{\sum_{k=1}^{\infty} \int_{\mathbb{R}^{6N}} \bar{f}_{kk}(z') dz'}, \end{aligned} \quad (5.21)$$

and $\bar{\sigma}(z^j; y, \tau)$ and $\bar{q}(z^j; y, \tau)$ are defined in (3.8) and (3.12), respectively, now using $\lambda = \bar{\lambda}_j$, and the matrix-valued symbols

$$\begin{aligned} \bar{\rho}_0 &= \sum_n \eta(y - x^n) \mathbf{I}, \\ \bar{p}_0 &= \sum_n \eta(y - x^n) p^n \mathbf{I}, \\ \bar{E}_0 &= \sum_n \eta(y - x^n) \left(\frac{|p^n|^2}{2} \mathbf{I} + \bar{\Lambda}^n(x) \right), \\ \bar{F}_0 &= \sum_n \eta(y - x^n) \nabla_{x^n} V_b(x) \mathbf{I}, \\ \bar{P}_0 &= \sum_n M_n^{-1} \eta(y - x^n) p^n \cdot \nabla_{x^n} V_b(x) \mathbf{I}. \end{aligned} \quad (5.22)$$

Proof. The quantum observables (5.19), based on the approximate electron operator V with finite d and positive parameter δ_a , satisfy the assumptions in Theorem 5.1 with η regularized as η_{δ_p} . These regularized quantum observables therefore have a classical limit as $M \rightarrow \infty$: given small positive (δ_a, δ_p) and large finite d, M , the leading order terms in the classical approximation are, by Theorem 5.1, arbitrarily close to the terms in (5.21) while the error term c/M can be made sufficiently small using sufficiently large M .

To verify that the observables satisfy the conservation laws, we need to take the limit $\delta_p \rightarrow 0+$ in both the quantum observables (5.19) and the leading order classical term (5.21), since the quantum conservation laws (5.8), (5.14) and (5.15) are given with $\delta_p = 0$. As $\delta_p \rightarrow 0+$, the regularized observables in (5.19), based on the positive δ_a , converge by Assumption 5.1 to the observables that satisfy the conservation laws (5.8), (5.14) and (5.15). Combined with the continuous dependence on $\delta_p \rightarrow 0+$ in the leading order terms of the molecular dynamics approximation (5.21) we obtain the consistency results (5.20)-(5.22). \square

The result of Theorem 5.2 still depends on the regularization parameters δ_a and d , while the ab initio model corresponds to $\delta_a = 0$ and $d = \infty$. The molecular dynamics observables in Theorem 5.2 are consistent with the ab initio quantum model in the sense that if the molecular dynamics observables in Theorem 5.2 and the $M \rightarrow \infty$ limits of the quantum observables in (5.19) have limits as $\delta_a \rightarrow 0+$ and $d \rightarrow \infty$, with the limits based on $\delta_a = 0$ and $d = \infty$, then the corresponding molecular dynamics and quantum limits are equal.

Theorem 5.2 proves in particular that the observables are determined by a weighted average with the probability q_j^* to be in state j . Using this probability model, the conservation laws (5.20) are consistent with the derivation of the conservation laws from the classical dynamics in Section 3.

5.3. General nuclei masses. In this section we describe how the general case of individual nuclei masses and a diagonal mass matrix M can be reduced to the case with equal masses by rescaling the nuclei position coordinates as $M_1^{1/2}x' = M^{1/2}x$, where $M_1 \gg 1$ is the mass of nuclei 1 acting as a reference mass. The change of variables $x(x')$ transforms the Laplacian $M^{-1}\mathbf{I}\Delta_x$ to $M_1^{-1}\mathbf{I}\Delta_{x'}$ so that in the coordinates x' the Hamiltonian has equal mass M_1 , namely

$$\begin{aligned} \hat{H} &= (2M)^{-1}\mathbf{I}\Delta_x + V(x) + V_b(x) \\ &= -(2M_1)^{-1}\mathbf{I}\Delta_{x'} + V(M_1^{1/2}M^{-1/2}x') + V_b(M_1^{1/2}M^{-1/2}x') \\ &= (2M_1)^{-1}\widehat{|p'|^2} + V(M_1^{1/2}M^{-1/2}x') + V_b(M_1^{1/2}M^{-1/2}x'). \end{aligned}$$

We can therefore perform the analysis as described in Sections 5.1 and 5.2 in the transformed coordinates (x', p') , with equal reference mass M_1 . Theorems 5.1 and 5.2 then provide the molecular dynamics approximation in the (x', p') coordinates.

The next step is to relate the obtained dynamics in the (x', p') coordinates to the original coordinates (x, p) , as follows. The classical limit is by Theorem 5.1 based on Lemma 4.1 applied to the Poisson bracket $\{\bar{H}(x', p'), \bar{A}(x(x'), p(p'))\}$ with \bar{A} given by the conservation variables (5.22), which takes the form $\{\bar{H}_{jj}(x', p'), \bar{A}_{jj}(x(x'), p(p'))\} = \{|p'|^2/2 + \bar{\lambda}_j(x(x')), \bar{A}_{jj}(x(x'), p(p'))\}$. Therefore Theorems 5.1 and 5.2 yield the molecular dynamics given by the transformed Hamiltonian system

$$\begin{aligned} \dot{x}'_\tau &= p'_\tau \\ \dot{p}'_\tau &= -\nabla_{x'}\bar{\lambda}_j(M_1^{1/2}M^{-1/2}x'_\tau) - \nabla_{x'}V_b(M_1^{1/2}M^{-1/2}x'_\tau), \quad \tau > 0. \end{aligned} \tag{5.23}$$

The change of variables $x = M_1^{1/2} M^{-1/2} x'$ and $\bar{p} = M_1^{1/2} M^{-1/2} p'$ implies that

$$\begin{aligned} \dot{x}_\tau &= \bar{p}_\tau \\ \dot{\bar{p}}_\tau &= -M_1 M^{-1} (\nabla_x \bar{\lambda}_j(x_\tau) + \nabla_x V_b(x_\tau)), \quad \tau > 0. \end{aligned} \tag{5.24}$$

Let $p = M_1^{-1/2} M \bar{p}$ and change to the fast time scale $t = M_1^{1/2} \tau$, then (5.24) is equivalent to the standard form

$$\begin{aligned} \dot{x}_t &= M^{-1} p_t \\ \dot{p}_t &= -\nabla_x \bar{\lambda}_j(x_t) - \nabla_x V_b(x_t), \quad t > 0, \end{aligned}$$

with individual masses in the diagonal mass matrix M , i.e. the molecular dynamics (5.23), obtained from the transformed system with equal mass, generates the standard form of molecular dynamics with individual masses.

5.4. Coinciding eigenvalues. The assumption on distinct eigenvalues in Theorem 5.1 is used in the proof to obtain differentiable eigenvalues and eigenvectors by regular perturbation theory in (5.3). To the authors' knowledge the classical limit of quantum observables in the canonical ensemble related to Theorem 5.1 in the case of degenerate eigenvalues is an open problem.

Here we speculate on how to relax the assumption on distinct eigenvalues for a special type of degeneracy.

The eigenvectors corresponding to λ_i and λ_{i+1} are typically not continuous at conical intersections x , where $\lambda_i(x) = \lambda_{i+1}(x)$, see e.g. [17, Section 12.2.3]. The proof of Theorem 5.1 uses the regularity of the eigenvectors of V only to obtain the solution of the approximate nonlinear eigenproblem (5.3).

Here we show that the approximate nonlinear diagonalization becomes surprisingly simple for the special example of a real valued 2×2 matrix $V = \begin{bmatrix} v_{11} & v_{12} \\ v_{12} & v_{22} \end{bmatrix}$, i.e. in the case of $d=2$. Its eigenvalues are $\lambda_\pm = \frac{v_{11} + v_{22}}{2} \pm r$, where the function $r: \mathbb{R}^{3N} \rightarrow \mathbb{R}$ is defined by $r := \sqrt{(\frac{v_{11} - v_{22}}{2})^2 + v_{12}^2}$ and when $r(x) = 0$ there is a conical intersection with $\lambda_+(x) = \lambda_-(x)$. Corresponding eigenvectors are given by

$$\Psi = \begin{bmatrix} \cos \alpha / 2 & \sin \alpha / 2 \\ -\sin \alpha / 2 & \cos \alpha / 2 \end{bmatrix}, \tag{5.25}$$

where

$$(\cos \alpha, \sin \alpha) = \left(\frac{v_{11} - v_{22}}{2r}, \frac{v_{12}}{r} \right), \quad \text{for } r \neq 0, \tag{5.26}$$

which locally yields a function α with the same regularity as V , for $r \neq 0$. Globally we may need a partition of unity with different charts to compute the gradient of Ψ . We have by (5.26)

$$V = \frac{v_{11} + v_{22}}{2} \mathbf{I} + r \begin{bmatrix} \cos \alpha & \sin \alpha \\ \sin \alpha & -\cos \alpha \end{bmatrix}.$$

Differentiating (5.25) gives

$$\nabla \Psi^* \cdot \nabla \Psi = \frac{|\nabla \alpha|^2}{4} \begin{bmatrix} -\sin \alpha / 2 & \cos \alpha / 2 \\ -\cos \alpha / 2 & -\sin \alpha / 2 \end{bmatrix}^* \begin{bmatrix} -\sin \alpha / 2 & \cos \alpha / 2 \\ -\cos \alpha / 2 & -\sin \alpha / 2 \end{bmatrix} = \frac{|\nabla \alpha|^2}{4} \mathbf{I} \tag{5.27}$$

and consequently

$$(V + \frac{1}{4M} \Psi \nabla \Psi^* \cdot \nabla \Psi \Psi^*) \Psi = \Psi (\Lambda + \frac{|\nabla \alpha|^2}{16M} \mathbf{I}) = \Psi \bar{\Lambda} \tag{5.28}$$

in fact solves the nonlinear eigenvalue problem (5.2) exactly for $r \neq 0$. For a calculation of $\nabla \alpha$ we introduce $\tilde{v} := \frac{v_{11} - v_{22}}{2}$ and note that $\tan \alpha = v_{12} / \tilde{v}$ so $\alpha = \tan^{-1} v_{12} / \tilde{v} + n\pi$ and $\nabla \alpha(x) = \frac{\tilde{v} \nabla v_{12} - v_{12} \nabla \tilde{v}}{\tilde{v}^2 + v_{12}^2}$. We note that the nonlinear eigenvalues $\bar{\lambda}_k$ have the additional term $|\nabla \alpha|^2 / (16M)$ which is large if r is small, i.e. in the potential landscape of $\bar{\lambda}_k$ the canonical ensemble weight $e^{-\bar{\lambda}_k / T}$ will vanish at the conical intersection where $r = 0$.

The observation that in the special case of $d=2$ the nonlinear eigenvalue problem (5.2) is diagonal in the sense of (5.28), could be the first step to extend Theorem 5.1 to include conical intersections with coinciding eigenvalues.

6. The initial particle density

Assume we know the initial data $(\rho(\cdot, 0), \rho u(\cdot, 0), E(\cdot, 0))$ for the macroscopic conservation laws, although in practise this data can be hard to determine, e.g. for the flow in a river. Current molecular dynamics simulations can only use a small fraction of the number of particles in a real system. Therefore we need an initial particle density that is related to a larger ensemble. We seek a density that has the property that the marginal distribution of a subsystem weakly coupled to a larger heat bath system is the same as the whole system. Under certain assumptions stated in [7], the classical Gibbs density is the only density with this property. Given the local values of the macroscopic conserved variables, the goal here is therefore to determine a local grand canonical Gibbs density

$$\bar{f}_{jj}(x, p; y) \sim e^{-\mathcal{H}(x, p, j; y) / T(y)} \tag{6.1}$$

where

$$\mathcal{H}(x, p, j; y) := \sum_{n=1}^N \eta(y - x^n) \left(\underbrace{\bar{H}^n(x, p, j)}_{= \frac{|p^n|^2}{2M_n} + \bar{\lambda}_j^n(x)} - M_n \mu(y) \right),$$

based on local values of the temperature $T(y)$ and the chemical potential $\mu(y)$, such that

$$\begin{pmatrix} \rho(y, 0) \\ \rho u(y, 0) \\ E(y, 0) \end{pmatrix} = (\text{Tr}(\hat{f}))^{-1} \text{Tr} \left(\begin{pmatrix} \hat{\rho}_0 \\ \hat{p}_0 \\ \hat{E}_0 \end{pmatrix} \hat{f} \right). \tag{6.2}$$

Weyl’s law given by the quantum-classical representation (5.16) combined with (6.2) show that the equation

$$\rho u(y, 0) = \frac{\int_{\mathbb{R}^{6N}} \sum_{n=1}^N \eta(y - x^n) p^n \sum_{j=1}^d \bar{f}_{jj}(x, p) dx dp}{\int_{\mathbb{R}^{6N}} \sum_{j=1}^d \bar{f}_{jj}(x, p) dx dp}$$

defines the initial velocity $u(y, 0)$. It remains to verify if varying $T(y)$ and $\mu(y)$ yield large enough sets to match the initial data for ρ and E .

If $|\mu(y)| \gg 1$ we roughly get $\mathcal{H} \simeq -\sum_{n=1}^N \eta(y - x^n) \mu(y)$. Laplace principle implies that as $\mu(y) \rightarrow -\infty$ the grand canonical density will sample the minimum of the observable $\sum_{n=1}^N \eta(y - x^n)$ and as $\mu(y) \rightarrow \infty$ the microscopic particle density will sample the

maximum of $\sum_{n=1}^N \eta(y-x^n)$. Therefore varying $\mu(y)$ from $-\infty$ to ∞ will change the local density

$$\rho(y,0) = \frac{\int_{\mathbb{R}^{6N}} \sum_{n=1}^N \eta(y-x^n) M_n \sum_{j=1}^d \bar{f}_{jj}(x,p) dx dp}{\int_{\mathbb{R}^{6N}} \sum_{j=1}^d \bar{f}_{jj}(x,p) dx dp}$$

from nearly vacuum to arbitrarily high macroscopic density.

The temperature is related to the microscopic kinetic energy and we have

$$E(y,0) = \frac{\int_{\mathbb{R}^{6N}} \sum_{n=1}^N \sum_{j=1}^d \eta(y-x^n) \left(\frac{|p^n|^2}{2M_n} + \bar{\lambda}_j^n(x) \right) \bar{f}_{jj}(x,p) dx dp}{\int_{\mathbb{R}^{6N}} \bar{f}_{jj}(x,p) dx dp}.$$

We see that the factor $\eta(y-x^n) \frac{|p^n|^2}{2M_n} e^{-\eta(y-x^n)|p^n|^2/(T(y)2M_n)}$ upon integration with respect to p^n will be proportional to $T(y)$. The other terms in $E(y,0)$ will have upper and lower bounds uniform in T . Therefore by varying the temperature a large open set of macroscopic energies can be attained.

Finally, we note that minimizing the entropy $\sum_{j=1}^d \int_{\mathbb{R}^{6N}} \bar{f}_{jj}(z) \log \bar{f}_{jj}(z) dz$ under the constraints that the value of the macroscopic density is $\rho(y,0)$ and the macroscopic energy is $E(y,0)$ yields the probability density

$$\bar{f}_{jj}(z) = c e^{-\sum_{n=1}^N \eta(y-x^n) M_n \mu_0(y) - \sum_{n=1}^N \eta(y-x^n) \bar{H}^n(z,j) \mu_1(y)} = c e^{-\mathcal{H}(z,j;y)/T(y)}$$

for $c = 1 / \sum_{j=1}^d \int_{\mathbb{R}^{6N}} e^{-\mathcal{H}(z,j;y)/T(y)} dz$ with the Lagrange multipliers $\mu_1(y) = 1/T(y)$ and $\mu_0(y) = \mu(y)/T(y)$. The Gibbs density (6.1) is therefore consistent with this constrained minimization.

7. The partial derivatives $\partial_{r^k} \tilde{\lambda}(\tilde{x})$

The function $\tilde{\lambda}$ is defined by (3.2) on the set $M \subset \mathbb{R}^{N(N-1)/2}$ consisting of all vectors $r := (r^{12}, r^{13}, \dots, r^{N-1N})$ such that there exist particle positions $x^i \in \mathbb{R}^3$, $i = 1, \dots, N$ and $r^{ij} = |x^i - x^j|$ for $1 \leq i < j \leq N$. The goal here is to define the gradient $\nabla_r \tilde{\lambda}$ such that the chain rule $\nabla \lambda(x) = (\partial r / \partial x)^T \nabla_r \tilde{\lambda}(r)$ is valid on M . We therefore need to solve the linear equation $Av = b$ for $v = \nabla_r \tilde{\lambda}$, where we have used the notation $A = (\partial r / \partial x)^T$ and $b = \nabla \lambda$. Since this is an underdetermined linear system we choose the solution v that minimizes the ℓ^2 norm. The stationary point to the Lagrangian $L(v, y) = |v|^2/2 + y \cdot (Av - b)$, where y is the Lagrange multiplier, has the solution

$$v = A^T (AA^T)^{-1} b. \tag{7.1}$$

Since generically the matrix A has full rank, Equation (7.1) contains a computable expression for $v = \nabla_r \tilde{\lambda}$, which can be used in the expression for the stress tensor in (3.8).

REFERENCES

- [1] N.C. Admal and E.B. Tadmor, *A unified interpretation of stress in molecular systems*, J. Elast., 100:63–143, 2010. [1](#), [3](#)
- [2] E. Cancés, M. Defranceschi, W. Kutzelnigg, C. Le Bris, and Y. Maday, *Computational quantum chemistry: a primer*, in Ph. Ciarlet and C. Le Bris (eds.), *Handbook of Numerical Analysis. Volume X: Computational Chemistry*, North-Holland, 3–270, 2003. [2.1](#), [2.1](#)
- [3] D. Frenkel and B. Smit, *Understanding Molecular Simulation*, Academic Press New York, 2002. [1](#)

- [4] R.J. Hardy, *Formulas for determining local properties in molecular dynamics simulations: Shock waves*, J. Chem. Phys., 76(1):622–628, 1982. [1](#), [2.2](#), [2.2.2](#), [3](#), [3.2](#), [3.3](#)
- [5] J.H. Irving and J.G. Kirkwood, *The statistical mechanical theory of transport processes. IV. The equations of hydrodynamics*, J. Chem. Phys., 18(6):817–829, 1950. [1](#), [2.2](#), [2.2.2](#), [3](#), [3.3](#)
- [6] J.H. Irving and R.W. Zwanzig, *The statistical mechanical theory of transport processes. V. Quantum hydrodynamics*, J. Chem. Phys., 19(9):1173–1180, 1951. [1](#), [2.2](#), [4](#)
- [7] A. Kammonen, P. Plecháč, M. Sandberg, and A. Szepessy, *Canonical quantum observables for molecular systems approximated by ab initio molecular dynamics*, Ann. Henri Poincaré 19:2727–2781, 2018. [1](#), [2.2.3](#), [5.1](#), [5.1](#), [5.1](#), [5.2](#), [6](#)
- [8] T. Kato, *Perturbation Theory for Linear Operators*, Springer-Verlag Berlin Heidelberg New York, 1980. [2.2.2](#)
- [9] C. LeBris, *Computational chemistry from the perspective of numerical analysis*, Acta Numer., 14:363–444, 2005. [2.1](#)
- [10] E. Lieb and R. Seiringer, *The Stability of Matter in Quantum Mechanics*, Cambridge University Press, 2010. [2.1](#), [2.1](#)
- [11] A. Martinez, *An Introduction to Semiclassical and Microlocal Analysis*, Springer-Verlag, 2002. [4](#)
- [12] V. Maz'ya and M. Shubin, *Discreteness of spectrum and positivity criteria for Schrödinger operators*, Ann. Math., 162:919–942, 2005. [2.2.3](#)
- [13] B. Nachtergaele and H.T. Yau, *Derivation of the Euler equations from quantum mechanics*, Commun. Math. Phys., 243:485–540, 2003. [1](#)
- [14] W. Noll, *Die Herleitung der Grundgleichungen der Thermomechanik der Kontinua aus der statistischen Mechanik*, J. Ration. Mech. Anal., 4:627–646, 1955. English translation in arXiv:0810.0337v3. [1](#), [2.2](#), [2.2.2](#), [3](#), [3.2](#), [3.2](#), [3.3](#)
- [15] S. Olla, S.R.S. Varadhan and H.T. Yau, *Hydrodynamical limit for a Hamiltonian system with weak noise*, Commun. Math. Phys., 155:523–560, 1993. [1](#), [2.2.2](#)
- [16] H.-M. Stiepan and S. Teufel, *Semiclassical approximations for Hamiltonians with operatorvalued symbols*, Comm. Math. Phys., 320(3):821–849, 2013. [1](#), [5.1](#), [5.2](#)
- [17] D.J. Tannor, *Introduction to Quantum Mechanics: A Time-Dependent Perspective*, University Science Books, 2007. [5.4](#)
- [18] J.Z. Yang, X. Wu, and X. Li, *A generalized Irving–Kirkwood formula for the calculation of stress in molecular dynamics models*, J. Chem. Phys., 137, 134104, 2012. [1](#)
- [19] E.B. Webb, J.A. Zimmerman, and S.C. Seel, *Reconsideration of continuum thermomechanical quantities in atomic scale simulations*, Math. Mech. Solids, 13:221–266, 2008. [1](#)
- [20] M. Zworski, *Semiclassical Analysis*, Amer. Math. Soc., Providence, RI, 2012. [4.1](#), [5.1](#)