STOCHASTIC AND DETERMINISTIC MOLECULAR DYNAMICS DERIVED FROM THE TIME-INDEPENDENT SCHRÖDINGER EQUATION

ANDERS SZEPESSY

ABSTRACT. Born-Oppenheimer, Smoluchowski, Langevin, Ehrenfest and surface-hopping dynamics are shown to be accurate approximations of time-independent Schrödinger observables for a molecular system, in the limit of large ratio of nuclei and electron masses, without assuming that the nuclei are localized to vanishing domains. The derivation, based on characteristics for the Schrödinger equation, bypasses the usual separation of nuclei and electron wave functions and gives a different perspective on initial and boundary conditions, caustics and irreversibility, the Born-Oppenheimer approximation, hopping, computation of observables and stochastic electron equilibrium states in molecular dynamics modeling.

Contents

1. The Schrödinger and Ehrenfest models 2
2. Ehrenfest dynamics derived from the time-independent Schrödinger equation 5
2.1. Exact Schrödinger dynamics 5
2.2. Irreversibility in Hamilton-Jacobi equations generated by shock waves 8
2.3. Approximate Ehrenfest dynamics and densities 12
2.4. Comparison of two alternative Ehrenfest formulations 13
2.5. Equations for the density 15
2.6. Construction of the solution operator 16
3. The time-dependent Schrödinger equation 17
4. Surface-hopping and multiple states 18
4.1. Surface-hopping and Ehrenfest dynamics for multiple states 18
4.2. Characteristics hopping in the Ehrenfest dynamics 19
5. Computation of observables 20
6. Approximation error derived from a Hamilton-Jacobi equation 22
6.1. The Ehrenfest approximation error 22
6.2. The Born-Oppenheimer approximation 25
6.3. Stochastic Langevin and Smoluchowski molecular dynamics approximation 26
7. Construction of the solution operator 32

2000 Mathematics Subject Classification. Primary: 81Q20; Secondary: 82C10.

Key words and phrases. Ehrenfest dynamics, quantum classical molecular dynamics, surface-hopping, foundations of quantum mechanics, WKB expansion, Born-Oppenheimer approximation, Langevin equation, Smoluchowski equation, Schrödinger equation, shock wave.
1. The Schrödinger and Ehrenfest models

The *time-independent* Schrödinger equation

\( H(x, X)\Phi(x, X) = E\Phi(x, X), \)

models nuclei-electron systems and is obtained from minimization of the energy in the solution space of wave functions, cf. [39, 4, 41, 10]. It is an eigenvalue problem for the energy \( E \in \mathbb{R} \) of the system in the solution space, described by wave functions, \( \Phi: \mathbb{R}^{3J} \times \mathbb{R}^{3N} \to \mathbb{C} \), depending on electron coordinates \( x = (x^1, \ldots, x^J) \in \mathbb{R}^{3J} \), nuclei coordinates \( X = (X^1, \ldots, X^N) \in \mathbb{R}^{3N} \), and a Hamiltonian operator \( H(x, X) \)

\[
H(x, X) = V(x, X) - \frac{1}{2M} \sum_{n=1}^{N} \Delta X^n.
\]

The nuclei masses \( M \) are assumed to be large and the interaction potential \( V \), independent of \( M \), is in the canonical setting (neglecting relativistic and magnetic effects),

\[
V(x, X) = -\frac{1}{2} \sum_{j=1}^{J} \Delta x^j + \sum_{1 \leq k < j \leq J} \frac{1}{|x^k - x^j|} - \sum_{n=1}^{N} \sum_{j=1}^{J} \frac{Z_n}{|x^j - X^n|} + \sum_{1 \leq n < m \leq N} \frac{Z_n Z_m}{|X^n - X^m|},
\]

composed of the kinetic energy of the electrons, the electron-electron repulsion, the electron-nuclei attraction, and the repulsion of nuclei (with charge \( Z_n \)), in the Hartree atomic units where the electron mass, electron charge, reduced Planck constant, and the Coulomb force constant \((4\pi\epsilon_0)^{-1}\) all are one. The mass of the nuclei, which are much greater than one (electron mass), are the diagonal elements in the diagonal matrix \( M \).

An essential feature of the partial differential equation (1.1) is the high computational complexity to determine the solution, in an antisymmetric/symmetric subset of the Sobolev space \( H^1(\mathbb{R}^{3(J+N)}) \). Wave functions depend also on discrete spin states

\[
\Phi(x^1, \sigma_1, \ldots, x^J, \sigma_J, X_1, \Sigma_1, \ldots, X_N, \Sigma_N),
\]

which effect the solutions space: each electron spin \( \sigma_j \) can take two different values and each nucleus can be in a finite set of spin states \( \Sigma_n \); the *Pauli exclusion principle* restricts the
solutions space to wave functions satisfying the antisymmetry/symmetry
\[ \Phi(\ldots, x^j, \sigma_j, \ldots, x^k, \sigma_k, \ldots) = -\Phi(\ldots, x^k, \sigma_k, \ldots, x^j, \sigma_j, \ldots) \]
for any \( 1 \leq j, k \leq J \)
and for any pair of nuclei \( n \) and \( m \), with \( A \) nucleons and the same number of protons and neutrons,
\[ \Phi(\ldots, X^m, \Sigma_m, \ldots, X^n, \Sigma_n, \ldots) = (-1)^A \Phi(\ldots, X^n, \Sigma_n, \ldots, X^m, \Sigma_m, \ldots) \]
cf. [10]. We simplify the notation by writing \( \Phi(x, X) \) instead of the more complete (1.3), since the Hamiltonian \( H \) does not depend on the spin of each particle. An attractive property of the Schrödinger equation (1.1) is the precise definition of the Hamiltonian and the solutions space, without unknown parameters, and its good agreement with experimental results. The agreement with measurements can be further improved by including relativistic and magnetic effects, cf. [10].

In contrast to the Schrödinger equation, a *molecular dynamics* model of nuclei \( X : [0, T] \rightarrow \mathbb{R}^{3N} \), with a given potential \( V_0 : \mathbb{R}^{3N} \rightarrow \mathbb{R} \), can be computationally studied also for large \( N \) by solving the ordinary differential equation
\[ M \ddot{X}_\tau = -\partial_X V_0(X_\tau). \] (1.4)
This computational and conceptual simplification motivates the study to determine the potential and its implied accuracy by a derivation of molecular dynamics from the Schrödinger equation, as started already in the 1920’s with the seminal Born-Oppenheimer approximation [7]. The purpose here is to contribute to the current understanding of such derivations, by showing improved convergence rates under new assumptions.

A useful sub step to derive molecular dynamics from the Schrödinger equation is * Ehrenfest dynamics*, for classical *ab initio* motion of the nuclei coupled to Schrödinger dynamics for the electrons,
\[ M \ddot{X}^n_\tau = -\int_{\mathbb{R}^{3J}} \phi^*_\tau(\cdot, X_\tau) \partial_{X^n} V(\cdot, X_\tau) \phi_\tau(\cdot, X_\tau) \, dx \]
\[ i \dot{\phi}_\tau = V(\cdot, X_\tau) \phi_\tau. \] (1.5)
The Ehrenfest dynamics (1.5) has been derived from the time-dependent Schrödinger equation through the self consistent field equations, see [8, 36, 42]. Equation (1.5) can be used for *ab initio* computation of molecular dynamics, cf. [36, 33]. A next step is the Born-Oppenheimer approximation, where \( X_\tau \) solves the classical *ab initio* molecular dynamics (1.4) with the potential \( V_0 : \mathbb{R}^{3N} \rightarrow \mathbb{R} \) determined as an eigenvalue of the electron Hamiltonian \( V(\cdot, X) \) for a given nuclei position \( X \), that is \( V(\cdot, X)\phi_0(X) = V_0(X)\phi_0(X) \), for instance with the electron ground state \( \phi_0(X) \). The Born-Oppenheimer approximation has been derived from the time-dependent Schrödinger equation in [24, 38].

The model (1.4) simulates dynamics at constant energy \( M |\dot{X}|^2/2 + V_0(X) \), constant number of particles \( N \) and constant volume, i.e. the microcanonical ensemble. The alternative to simulate with constant number of particles, constant volume and constant temperature \( T \),
i.e. the canonical ensemble, is possible for instance with the stochastic Langevin dynamics
\begin{equation}
\begin{aligned}
\frac{dX}{\tau} &= v_{\tau} d\tau \\
Mdv_{\tau} &= -\partial_{X} V_{0}(X_{\tau}) d\tau - K v_{\tau} d\tau + (2TK)^{1/2} dW_{\tau},
\end{aligned}
\end{equation}

where \(W_{\tau}\) is the standard Brownian process (at time \(\tau\)) in \(\mathbb{R}^{3N}\) with independent components and \(K\) is a positive friction parameter. When the observable only depends on the nuclei positions, i.e. not on the nuclei velocities or the correlation of positions at different times, the Smoluchowski dynamics
\begin{equation}
\begin{aligned}
\frac{dX}{\tau} &= -\partial_{X} V_{0}(X_{\tau}) + (2T)^{1/2} dW_{\tau}
\end{aligned}
\end{equation}
is a simplified alternative to Langevin dynamics, cf. [9].

This paper derives the Ehrenfest dynamics (1.5) and the Born-Oppenheimer approximation from the time-independent Schrödinger equation (1.1). The time-independent Schrödinger equation has convincing agreement with experimental results, as the basis for computational chemistry and solid state physics. The time-dependent Schrödinger equation on the other hand is less well established from experiments and that motivates also to present a derivation of molecular dynamics from the time-independent Schrödinger equation, although the main point here is to show improved convergence rates under simple assumptions.

The main idea in this paper, inspired by [37, 5, 6], is to introduce the time-dependence from the classical characteristics in the Hamilton-Jacobi equation obtained by writing the time-independent eigenfunction (1.1) in WKB-form. The work [37, 5, 6] derives the time-dependent Schrödinger dynamics of an \(x\)-system, \(i\dot{\Psi} = H_{1}\Psi\), from the time-independent Schrödinger equation (with the Hamiltonian \(H_{1}(x) + \delta H(x,X)\)) by a classical limit for the environment variable \(X\), as the coupling parameter \(\delta\) vanishes and the mass \(M\) tends to infinity; in particular [37, 5, 6] show that the time derivative enters through the coupling of \(\Psi\) with the classical velocity.

Here we refine the use of characteristics to study classical \textit{ab initio} molecular dynamics, where the coupling does not vanish, and we establish error estimates for Born-Oppenheimer, Ehrenfest, surface-hopping and stochastic approximations of Schrödinger observables. The small scale, introduced by the perturbation \(- (2M)^{-1} \sum_{n} \Delta_{X_{n}}\) of the potential \(V\), is identified in a standard WKB eikonal equation, while its transport equation is analyzed as a time-dependent Schrödinger equation along characteristics, instead of as a usual series expansion [26]. The analysis based on the characteristics for the time-independent Schrödinger equation, bypasses the usual separation of nuclei and electron wave functions in the time-dependent self consistent field equations [8, 36, 42]. The characteristic particle paths that may or may not return to the inflow domain, gives a different perspective on initial and boundary conditions, caustics and irreversibility, the Born-Oppenheimer approximation, hopping, and computation of observables. Section 3 shows that the Ehrenfest and surface-hopping dynamics are the same when derived from the time-independent and time-dependent Schrödinger equations.

Theorems 6.1 and 6.3 present conditions for approximating observables from the Schrödinger equation by observables from the Ehrenfest dynamics and the Born-Oppenheimer dynamics.
with error $O(M^{-1})$ respectively $O(M^{-1/2})$, using that these approximate solutions generate approximate eigenstates to the Schrödinger equation. The derivation does not assume that the nuclei are supported on small domains; in contrast, derivations based on the time-dependent self consistent field equations require nuclei to be supported on small domains. The reason that small support is not needed here comes from the combination of the characteristics and sampling from an equilibrium density, that is, for large $M$ the nuclei paths behave classically although they may not be supported on small domains. A large nuclei system, $N \gg M$, is used in Remark 6.2 to motivate an assumption on perturbations of the solutions to the Schrödinger equation (1.1). The derived approximation rates improve the previous $O(M^{-1/2})$ rate for Ehrenfest [8] and $O(M^{-1/4})$ rate for the zero order Born-Oppeneheimer approximation [24].

Section 6.3 applies the Ehrenfest approximation result to derive the Langevin and Smoluchowski dynamics from the Ehrenfest dynamics, when the electron state is stochastic perturbed from its ground state and the observable depends only on the nuclei positions but not their correlation at different time. The derivation uses a classical equilibrium Gibbs-Boltzmann distribution for the electron states and an assumption of a spectral gap, showing in Theorem 6.6 that observables of Langevin and Smoluchowski dynamics accurately approximate such Schrödinger observables. The main idea in the theorem is the non-standard view of a classical Gibbs-Boltzmann equilibrium distribution of electrons states, motivated by nuclei acting as heat bath for the electrons in the Ehrenfest Hamiltonian system.

It is my hope that the ideas in this paper stimulates more research on the conditions for molecular dynamics approximation. In particular it would be desirable to

- have more explicit conditions for the $L^2(dx,dX)$-bound on the $X$-Laplacian of the Ehrenfest electron wave function in (6.3), used in the approximation results and motivated in Remark 6.2, and
- further investigate the irreversibility of molecular dynamics caused by colliding characteristic paths, presented in Section 2.2.

2. Ehrenfest dynamics derived from the time-independent Schrödinger equation

2.1. Exact Schrödinger dynamics. Assume for simplicity that all nuclei have the same mass.\(^1\) The singular perturbation $-(2M)^{-1} \sum \Delta x_n$ of the potential $V$ introduces an additional small scale $M^{-1/2}$ of high frequency oscillations, as shown by a WKB-expansion, see [26, 12]. We will construct solutions to (1.1) in such WKB-form

\[
\Phi(x, X) = \psi_n(x, X) e^{i M^{1/2} \theta_n(X)},
\]

\(^1\)If this is not the case, change to new coordinates $M_1^{1/2} \tilde{X}_k = M_k^{1/2} X^k$, which transform the Hamiltonian to the form we want $V(x, M_1^{1/2} M^{-1/2} \tilde{X}) = \frac{1}{2M_1} \sum_{n=1}^N \Delta \tilde{x}_n$.\]
where the wave function $\psi_n$ is complex valued, the phase $\theta_n$ is real valued and the factor $M^{1/2}$ is introduced to have well defined limits of $\psi_n$ and $\theta_n$ as $M \to \infty$. The standard WKB-construction [26] is based on a series expansion in powers of $M^{1/2}$, we introduce instead a time-dependent Schrödinger transport equation. In the next section we use a linear combination of such eigensolutions - therefore the index $n$ is introduced. The Schrödinger equation (1.1) implies that

$$0 = (H - E)\psi_n e^{iM^{1/2}\theta_n(X)}$$

(2.2)

$$= \left(\frac{|\partial_X \theta_n|^2}{2} + V - E\right)\psi_n$$

$$- \frac{1}{2M} \sum_j \Delta_{Xj} \psi_n - \frac{i}{M^{1/2}} \sum_j (\partial_X \psi_n \partial_{Xj} \theta_n + \frac{1}{2} \psi_n \partial_{Xj} \theta_n) e^{iM^{1/2}\theta_n(X)}.$$  

Introduce the complex-valued scalar product

$$v \cdot w := \int_{\mathbb{R}^3} v(x, \cdot)^* w(x, \cdot) dx \equiv \langle v | w \rangle$$

on $L^2(\mathbb{R}^3)$ and the notation $X \circ Y$ for the standard scalar product on $\mathbb{R}^{3N}$. To find an equation for $\theta_n$, multiply (2.2) by $\psi_n^*$ and integrate over $\mathbb{R}^{3J}$; similarly take the complex conjugate of (2.2), multiply by $\psi_n$ and integrate over $\mathbb{R}^{3J}$; and finally add the two expressions to obtain

$$0 = 2\left(\frac{|\partial_X \theta_n|^2}{2} - E\right)\psi_n \cdot \psi_n + \psi_n \cdot V \psi_n + V \psi_n \cdot \psi_n = 2\psi_n \cdot V \psi_n$$

$$- \frac{1}{2M} \left(\psi_n \cdot \left(\sum_j \Delta_{Xj} \psi_n\right) + \left(\sum_j \Delta_{Xj} \psi_n\right) \cdot \psi_n\right)$$

(2.3)

$$+ \frac{i}{M^{1/2}} \left(\psi_n \cdot \left(\partial_X \psi_n \circ \partial_X \theta_n\right) - \left(\partial_X \psi_n \circ \partial_X \theta_n\right) \cdot \psi_n\right)$$

$$+ \frac{i}{2M^{1/2}} \left(\left(\psi_n \cdot \psi_n - \psi_n \cdot \psi_n\right) \sum_j \partial_{Xj} \theta_n\right).$$

The purpose of the phase function $\theta_n$ is to generate an accurate approximation in the limit as $M \to \infty$: therefore we define $\theta_n$ by the formal limit of (2.3) as $M \to \infty$, which is the Hamilton-Jacobi equation (also called the eikonal equation)

$$\frac{|\partial_X \theta_n|^2}{2} = E - V_n,$$

(2.4)

where the function $V_n : \mathbb{R}^{3N} \to \mathbb{R}$ is

$$V_n := \frac{\psi_n \cdot V \psi_n}{\psi_n \cdot \psi_n}.$$
Define also the density function \(\rho := \psi_n \cdot \psi_n\). For the energy \(E\) chosen larger than the potential energy, that is such that \(E \geq V_n\), the method of characteristics, cf. [16],

\[
\begin{align*}
\frac{dX_t}{dt} &= \partial_X \theta_n(X_t) =: p_t, \\
\frac{dp_t}{dt} &= -\partial_X V_n(X_t), \\
\frac{dz_t}{dt} &= |p_t|^2 = 2(E - V_n(X_t)),
\end{align*}
\]

yields a solution \((X, p, z) : [0, T] \rightarrow U \times \mathbb{R}^{3N} \times \mathbb{R}\) to the eikonal equation (2.4) locally in a neighborhood \(U \subseteq \mathbb{R}^{3N}\), for regular compatible data \((X_0, p_0, z_0)\) given on a \(3N - 1\) dimensional inflow-domain \(I \subset U\); here \(z_t := \theta_n(X_t)\). The work [26] proves the existence of a \(C^\infty\) solution \(\theta_n\) to the eikonal equation (2.4) in a neighborhood of a global minimum point of a given \(C^\infty\) non negative potential \(E - V_n : \mathbb{R}^{3N} \rightarrow [0, \infty)\); this handles the type of caustic (i.e. colliding characteristics) where \(\partial_X \theta_n\) vanishes. The phase function \(\theta_n : U \rightarrow \mathbb{R}\) becomes globally defined in \(U \subset \mathbb{R}^{3N}\) for instance when there is a unique characteristic path \(X_t\) going through each point in \(U\). Section 2.2 presents conditions for the case when characteristic paths collide, that lead to irreversible molecular dynamics.

Definition (2.4) implies that \(\psi_n\) solves the so called transport equation

\[
(2.6) \quad -\frac{1}{2M} \sum_j \Delta_{X_j} \psi_n + (V - V_n)\psi_n = \frac{i}{M^{1/2}} \sum_j \left( \partial_{X_j} \psi_n \partial_{X_j} \theta_n + \frac{1}{2} \partial_{X_j X_j} \theta_n \psi_n \right).
\]

Time enters into the Schrödinger equation through the characteristics and the chain rule

\[
\partial_X \psi_n \circ \partial_X \theta_n = \partial_X \psi_n \circ \frac{dx_t}{dt} = \frac{d\psi_n(x, X_t)}{dt},
\]

cf. [37, 5, 6]. Chose a coordinate system with the \(X_1^1\)-direction parallel to the momentum \(p = (p_1, 0, \ldots, 0)\) to evaluate the divergence

\[
(2.7) \quad \sum_j \partial_{X_j X_j} \theta_n = \text{div } p = \frac{\partial p_1}{\partial X_1^1} = \frac{\partial p_1}{\partial x_1^1} = \frac{\dot{p}_1}{p_1} = \frac{d}{dt} \frac{|p|^2}{2|p|^2} = \frac{d}{dt} \log |p|
\]

which leads to the integrating factor \(G_t := \sqrt{|p_t|}\) with the time derivative

\[
\dot{G} = \frac{d}{dt} \frac{|p|}{2|p|} = \frac{G}{2} \text{div } p;
\]

here our derivation differs from [37, 5, 6] which approximates the last term in (2.6),

\[
\sum_j \partial_{X_j X_j} \theta_n \psi_n,
\]

by zero in their case of vanishing coupling between the quantum system and the environment; here the coupling between the nuclei and electrons does not vanish. The right hand side
in (2.6) becomes the time derivative $iM^{-1/2}G^{-1} \frac{d(G\psi_n)}{dt}$ and we have derived the time-dependent Schrödinger equation, for the variable $\tilde{\psi}_n := G\psi_n$,

$$0 = (H - E)\Phi = \left( -\frac{i}{M^{1/2}}\dot{\psi}_n + (V - V_n)\tilde{\psi}_n - \frac{1}{2M} \sum_j G\Delta_{Xj}(\tilde{\psi}_n G^{-1}) \right) G^{-1}$$

$$+ \left( \frac{|\partial_X\theta_n|^2}{2} + V_n - E \right) \psi_n \right) e^{iM^{1/2}\theta_n(x)}. $$

(2.8)

The density can be written

$$\rho = \int_{\mathbb{R}^3} |\psi_n|^2 dx = \int_{\mathbb{R}^3} |\tilde{\psi}_n|^2 dx / G^2$$

and therefore the second equation in (2.5) yields the nuclei dynamics

$$\ddot{X} = -\partial_X \frac{\tilde{\psi}_n \cdot \tilde{V}_n \tilde{\psi}_n}{\tilde{\psi}_n \cdot \tilde{\psi}_n}.$$ 

In conclusion, we have derived the exact Schrödinger dynamics along the characteristics

$$\frac{i}{M^{1/2}}\dot{\psi}_n = (V - V_n)\tilde{\psi}_n - \frac{1}{2M} \sum_j G\Delta_{Xj}(\tilde{\psi}/G),$$

$$\ddot{X} = -\partial_X \frac{\tilde{\psi}_n \cdot \tilde{V}_n \tilde{\psi}_n}{\tilde{\psi}_n \cdot \tilde{\psi}_n}. $$

(2.9)

The derivatives $\partial_X G$ and $\partial_{XX} G$ can be determined from $(p, \partial_X p, \partial_{XX} p)$, which satisfy the following characteristic equations obtained from $X$-differentiation of (2.4)

$$\frac{d}{dt} \partial_{XX} p^k = \left[ \sum_j p^j \partial_{Xj} X^k p^j = \sum_j p^j \partial_{XX} X^k p^j \right]$$

$$= -\sum_j \partial_X p^j \partial_{XX} p^j - \partial_{XXX} X^k V_n,$$

(2.10)

$$\frac{d}{dt} \partial_{X^k} X^q p^k = \left[ \sum_j p^j \partial_{Xj} X^k X^q p^j = \sum_j p^j \partial_{X^k X^q} X^j p^j \right]$$

$$= -\sum_j \partial_X p^j \partial_{X^k} X^q p^j - \sum_j \partial_{X^k} X^q p^j \partial_X p^j - \partial_{X^k X^q} X^j V_n.$$ 

2.2. Irreversibility in Hamilton-Jacobi equations generated by shock waves. We will here show that colliding characteristic paths lead to irreversible Ehrenfest dynamics, although it is a Hamiltonian system. We will do that by requiring stability of the Hamilton-Jacobi and Schrödinger system (2.9) for a case with colliding characteristic paths.
We do not need a unique solution of the Hamilton-Jacobi equation, since we study an eigenvalue problem with multiple solutions, but we want to sort out stable solutions: if the data for $\theta_n$ and $\psi_n$ is slightly perturbed in the maximum norm, there should be a solution $\theta_n$ and $\psi_n$ which is close to the non perturbed solution in maximum norm. A stable generalized solution to the Hamilton-Jacobi equation with colliding paths can be irreversible in the sense that the solution is only stable when the initial data is given and not the final data, as explained in the example below.

At a point $X$ of two colliding characteristic paths, $(X, p^-, z^-)$ and $(X, p^+, z^+)$, we need first that

\begin{equation}
\text{the constructed phase } \theta_n \text{ is continuous, i.e. } z^- = z^+.
\end{equation}

Typically this condition yields a co-dimension one surface $\Gamma$ in $\mathbb{R}^{3N}$ (called a shock wave) where the characteristic paths collide; at the other points in $\mathbb{R}^{3N} \setminus \Gamma$ the characteristic paths do not collide. Secondly, to have a stable solution $\psi_n = |p|^{-1/2}\tilde{\psi}_n$, the right hand side in the Schrödinger equation (2.9)

\begin{equation}
\frac{i}{M^{1/2}} \tilde{\psi}_n = (V - V_n)\tilde{\psi}_n - \frac{|p|^{1/2}}{2M} \sum_j \Delta_{X_j}(|p|^{-1/2}\tilde{\psi}_n),
\end{equation}

has to be well behaved in the neighborhood of $\Gamma$, which excludes jumps in $|p|$; to have such jumps in $p$ means that the Hamiltonian is continuous, i.e.

\begin{equation}
|p^+|^2 = |p^-|^2.
\end{equation}

At the collision surface $\Gamma$, the Schrödinger equation (2.12) then has a right hand side where the function $|p|$ satisfies

\begin{align*}
|p^+|^{-1/2} &= |p^-|^{-1/2} \\
\partial_{X_j}|p^+|^{-1/2} &= \partial_{X_j}|p^-|^{-1/2} \\
\Delta_{X_j}|p^+|^{-1/2} &= \Delta_{X_j}|p^-|^{-1/2},
\end{align*}

so that although $p$ has a jump, the function $|p|$ is smooth in a neighborhood of $\Gamma$. The solution $\psi_n$ is therefore bounded also in a neighborhood of $\Gamma$. The requirement to satisfy the jump condition (2.13) is also one of the necessary conditions for unique so called viscosity solutions of Hamilton-Jacobi equations, see [16], but (2.13) and (2.11) are not enough, see the example below. Our third condition is to require that

\begin{equation}
\text{the solution } \theta_n \text{ is maximum norm stable towards perturbations of the initial data.}
\end{equation}

To more precisely define irreversibility we will use an example. We seek stable solutions to the Hamilton-Jacobi equation $F(\partial_X \theta(X), X) = 0$, using its Hamiltonian system

\begin{align*}
\dot{X}_t &= p_t \\
\dot{p}_t &= -\partial_X V(X_t),
\end{align*}
which has formally reversible solutions: for \( T > 0 \), the initial data \( p_0(X_0) \) determines \((X_T, p_T)\), which is the same as \((X_{-T}, -p_{-T})\) determined from the final data \(-p_0(X_0)\).

Consider the Hamilton-Jacobi equation \( p_1^2 + p_2^2 - 2 = 0 \) in the domain \( U = \mathbb{R} \times [-1, 0] \), in \( \mathbb{R}^2 \), with the associated Hamiltonian system

\[
\begin{align*}
\dot{X}_t &= p_t \\
\dot{p}_t &= 0.
\end{align*}
\]

This Hamilton-Jacobi equation has the stable initial-value solution

\[
p_1 = \begin{cases} 
  1 & X_1 < 0 \\
  -1 & X_1 > 0,
\end{cases}
\]

\[ p_2 = 1 \tag{2.15} \]

and the colliding characteristic paths satisfy the jump condition

\[ |p^-| = |p^+| \text{ at } \Gamma = \{0\} \times [-1, 0]. \]

The corresponding reversed final-value solution

\[
p_1 = \begin{cases} 
  -1 & X_1 < 0 \\
  1 & X_1 > 0,
\end{cases}
\]

\[ p_2 = -1, \tag{2.16} \]

which also satisfies \(|p^-| = |p^+|\) at \( \Gamma \), is unstable with respect to perturbations in the final value data: the regularized perturbed boundary data

\[
p_1 = \begin{cases} 
  -1 & X_1 < -\delta \\
  \delta^{-1}X_1 & -\delta < X_1 < \delta \\
  1 & X_1 > \delta,
\end{cases}
\]

\[ p_2 = -1, \]

as final value at the the inflow domain \( X_2 = 0 \), leads to the different stable final-value solution

\[ p(X_t) = p(X_0) = (p_1(y, 0), -\sqrt{2 - p_1(y, 0)^2}) \]

\[ X_t = X_0 + tp(X_0) \quad t < 0, \]

with no jump in \( p \), so in particular this \( p \) is not the negative of (2.15) as required for reversibility. The two stable solutions (2.15) and (2.16) are examples of a shock wave and a rarefaction wave, respectively, cf. [16]. Requiring such stability, solutions of the Hamilton-Jacobi equation and solutions to the corresponding Hamiltonian system are not reversible with respect to giving initial and final condition. In this sense, the molecular dynamics model (2.9) is time-irreversible.

The solution of the Hamilton-Jacobi equation, satisfying the three conditions (2.11), (2.13) and (2.14), is in fact the unique viscosity solution of

\[
F(\partial X \theta(X), X) := |\partial X \theta(X)|^2/2 + V(X) - E = 0 \quad \text{for } X \in U,
\]

\[ \theta(X) = g(X) \text{ or } F(\partial X \theta(X), X) = 0 \text{ for } X \in \partial U \]
for given functions $V : \mathbb{R}^{3N} \to \mathbb{R}$ and $g : \mathbb{R}^{3N} \to \mathbb{R}$; the stability holds with respect to perturbations in the boundary data $g$ and the potential $V$, in the maximum norm, and with respect to the domain $U$, see [2], [3] and [16]. The stable solution to the final-value problem, $(X_{-T}, -p_{-T})$, with respect to perturbations in the final data $p_0(X_0)$, can therefore be characterized by the optimal control problem
\[
\theta_f(Y) = \inf_{X_{-T} = Y, T > 0} \left( \int_{-T}^{0} \frac{|\dot{X}_t|^2}{2} - V(X) + E \, dt - g(X_0) \right),
\]
where $t = 0$ is the time a path $X_t$, starting at time $t = -T$ in $X_{-T} = Y \in U$, reaches the boundary $\partial U$; this viscosity solution can also be described as the vanishing viscosity solution, i.e. $\theta_f = \lim_{\epsilon \to 0^+} \theta^{\epsilon}$ where
\[
-F(\partial_X \theta^{\epsilon}(X), X) + \epsilon \sum_j \Delta X_j \theta^{\epsilon}(X) = 0 \quad X \in U
\]
\[
\theta^{\epsilon}(X) = -g(X) \quad X \in \partial U,
\]
cf. [2], [3] and [16]. Analogously, the stable solution to the initial value problem $(X_T, p_T)$, with respect to perturbations in the initial data $p_0(X_0)$, is the corresponding viscosity solution $\theta_i$ to $F(\partial_X \theta_i(X), X) = 0$, which can be characterized by the optimal control problem
\[
\theta_i(Y) = \inf_{X_t = Y, T > 0} \left( \int_{0}^{T} \frac{|\dot{X}_t|^2}{2} - V(X) + E \, dt + g(X_0) \right),
\]
or by the vanishing viscosity limit $\theta_i = \lim_{\epsilon \to 0^+} \theta^{\epsilon}$ where
\[
-F(\partial_X \theta^{\epsilon}(X), X) - \epsilon \sum_j \Delta X_j \theta^{\epsilon}(X) = 0 \quad X \in U
\]
\[
\theta^{\epsilon}(X) = g(X) \quad X \in \partial U.
\]
The example showed that $\theta_f(X) \neq -\theta_i(X)$ and hence stable solutions can be time-irreversible by only requiring stability with respect to perturbations in the initial data; the obtained viscosity solution of the Hamilton-Jacobi equation is then a consequence of this stability requirement.

We end the section by two examples of more complicated collisions. If characteristic paths collide, they may form closed curves $\tilde{\Gamma}$ containing crossing points and to avoid multiple values of $\theta_n$ we need that the corresponding integral satisfies
\[
\int_{a}^{b} p \circ p \, dt = \oint_{\tilde{\Gamma}} p \circ dX = 0,
\]
which follows by Stokes theorem since $p = \partial_X \theta_n$ locally. When three characteristic paths, $X^+, X^-$ and $X^0$ collide into a point it yields a collision of three shock waves. The codimension one surface $\Gamma$ in $\mathbb{R}^{3N}$ consists now of three parts, which intersect where the three paths have the same value of $\theta_n$. The three parts are generated, as in above, by the $\theta_n$-value attained by two paths $X^+ & X^-$, $X^+ & X^0$, and $X^- & X^0$, respectively. This can be generalized to up to $3N + 1$ colliding paths.
2.3. Approximate Ehrenfest dynamics and densities. We define the approximating Ehrenfest dynamics by in (2.2) neglecting the kinetic nuclei term

\[ 0 = \left( \frac{|\partial_X \hat{\theta}_n|^2}{2} + V - E \right) \hat{\psi}_n - \frac{i}{M^{1/2}} \sum_j (\partial_X \hat{\psi}_n \partial_X \hat{\theta}_n + \frac{1}{2} \hat{\psi}_n \partial_X \hat{\psi}_n \hat{\theta}_n), \]

and seek, as in (2.4), the approximate phase \( \hat{\theta}_n \) as the solution to eikonal equation

\[ \frac{|\partial_X \hat{\theta}_n|^2}{2} = E - \hat{V}_n, \]

where

\[ \hat{V}_n := \hat{\psi}_n \cdot V \hat{\psi}_n. \]

Introduce its characteristics

\[ \frac{d\hat{X}_t}{dt} = \partial_X \hat{\theta}_n(X_t) =: \hat{p}_t, \]
\[ \frac{d\hat{p}_t}{dt} = -\partial_X \hat{V}_n(\hat{X}_t), \]
\[ \frac{d\hat{z}_t}{dt} = |\hat{p}_t|^2 = -\hat{V}_n(\hat{X}_t), \]

to rewrite (2.17), as in (2.8),

\[ 0 = -\left( \frac{i}{M^{1/2}} \hat{\psi}_n - (V - \hat{V}_n) \hat{\psi}_n \right) \hat{G}^{-1} \left( \frac{|\partial_X \hat{\theta}_n|^2}{2} + V_n - E \right) \hat{\psi}_n, \]

\[ \hat{X} = -\frac{\partial_X (\hat{\psi}_n \cdot \hat{V}_n \hat{\psi}_n)}{\hat{\psi}_n \cdot \hat{\psi}_n}, \]

for \( \hat{\psi}_n := \hat{G} \hat{\psi}_n \) approximating \( \tilde{\psi}_n \) and \( \hat{G} := \sqrt{|\hat{p}_t|} \) as in (2.7). Using that \( \hat{\psi}_n \cdot \hat{\psi}_n \) is conserved (i.e. time-independent) in the Ehrenfest dynamics, we can normalize to \( \hat{\psi}_n \cdot \hat{\psi}_n = 1 \). Note that in the exact dynamics, the function \( \tilde{\psi}_n \cdot \tilde{\psi}_n \) is not conserved, due to the \( L^2(\mathbb{R}^3) \) non-Hermitian source term \( \frac{1}{2M} \sum_j G \Delta_{X_j} (\tilde{\psi}_n/G) \) in (2.9). We have

\[ V_n = \frac{\psi_n \cdot V \tilde{\psi}_n}{\psi_n \cdot \tilde{\psi}_n} = \frac{\tilde{\psi}_n \cdot V \tilde{\psi}_n}{\tilde{\psi}_n \cdot \tilde{\psi}_n} \]

and

\[ \hat{V}_n = \frac{\hat{\psi}_n \cdot \hat{V} \hat{\psi}_n}{\hat{\psi}_n \cdot \hat{\psi}_n} = \hat{\psi}_n \cdot V \hat{\psi}_n. \]
2.4. **Comparison of two alternative Ehrenfest formulations.** The Ehrenfest dynamics (2.19) and (1.5) differ in

1. the time scales \( t \) respectively \( M^{1/2} t = \tau \);
2. the potentials \( V - V_n \) and \( V \) in the equations for \( \hat{\psi}_n \) and \( \hat{\phi}_n \), respectively; and
3. the forces \( \partial_X(\hat{\psi}_n \cdot V \hat{\psi}_n) \) respectively \( \partial_X V \hat{\phi}_n \) in the momentum equation.

If \( \hat{\psi}_n \) solves (2.19), the change of variables

\[
\hat{\phi}_n = \hat{\psi}_n e^{-iM^{1/2} \int_0^t \hat{\psi}_n V \hat{\psi}_n (X_s) \, ds}
\]

and the property \( \hat{\psi}_n \cdot A \hat{\psi}_n = \hat{\phi}_n \cdot A \hat{\phi}_n \), which holds for any observable \( A \) independent of the nuclei momentum \( i\partial_X \) (in particular \( A = V_n \)), imply that \( \hat{\phi}_n \) solves

\[
\frac{i}{M^{1/2}} \hat{\phi}_n = V \hat{\phi}_n, \quad \ddot{X} = -\frac{\partial_X (\hat{\phi}_n \cdot \hat{V}_n \hat{\phi}_n)}{\hat{\phi}_n \cdot \hat{\phi}_n}.
\]

There has been a discussion in the literature \([8, 42]\) whether the forces should be computed as above in (2.20) or as in (1.5) by

\[
M \ddot{X}_r = -\int_{\mathbb{R}^3} \phi_r^*(\cdot, X_r) \partial_X V(\cdot, X_r) \phi_r(\cdot, X_r) \, dx
\]

\[
i \dot{\phi}_r = V(\cdot, X_r) \phi_r.
\]

The work \([43]\) points out that the two forces are the same in the direction of \( p(X_r) \), that is

\[
p(X_r) \circ \left( \int_{\mathbb{R}^3} \phi_r^* \partial_X V(\cdot, X_r) \phi_r \, dx - \partial_X \int_{\mathbb{R}^3} \phi_r^* (\cdot, X_r) V(\cdot, X_r) \phi_r (\cdot, X_r) \, dx \right) = 0.
\]

Equation (6.5) show that both formulations (2.20) and (2.21, 1.5) yield accurate approximations of the Schrödinger observables, although they are not the same. The reason that both approximations are accurate is that the two different characteristic systems solve the same Hamilton-Jacobi equation, as explained below and in Section 6.

The formulation (1.5) and (2.21) has the advantage to be a closed Hamiltonian system: the variable \((X, \varphi_r; p, \varphi_i)\), with the definition

\[
\varphi := \varphi_r + i \varphi_i := 2^{1/2} M^{-1/4} \phi = 2^{1/2} M^{-1/4} (\varphi_r + i \varphi_i),
\]

\[
\partial_{\varphi_r} \dot{\theta}_n := \varphi_i,
\]
and the Ansatz $\tilde{\theta} = \hat{\theta}$ imply that the Hamilton-Jacobi equation (2.18) becomes

\[
H_E := \frac{1}{2} \partial_X \tilde{\theta}_n \circ \partial_X \tilde{\theta}_n + \phi_r \cdot V(X) \phi_r + \phi_i \cdot V(X) \phi_i \\
= \frac{1}{2} \partial_X \tilde{\theta}_n \circ \partial_X \tilde{\theta}_n + 2^{-1} M^{1/2} \phi_r \cdot V(X) \phi_r + 2^{-1} M^{1/2} \phi_i \cdot V(X) \phi_i \\
= \frac{1}{2} \partial_X \tilde{\theta}_n \circ \partial_X \tilde{\theta}_n + 2^{-1} M^{1/2} \phi_r \cdot V(X) \phi_r + 2^{-1} M^{1/2} \partial_{\phi_r} \tilde{\theta}_n \cdot V(X) \partial_{\phi_r} \tilde{\theta}_n \\
= E,
\]

where the derivative $\partial_{\varphi_r} \tilde{\theta}(X, \varphi_r) = \varphi_i$, of the functional $\tilde{\theta} : \mathbb{R}^{3N} \times L^2(dx) \to \mathbb{R}$, is the Gateaux derivative in $L^2(dx)$. Its characteristics form the Hamiltonian system

\[
\begin{align*}
\dot{X}_t &= p_t \\
\dot{p}_t &= -\frac{M^{1/2}}{2} \varphi(t) \cdot \partial_X V(X) \varphi(t) \\
\varphi_r(t) &= M^{1/2} V(X) \varphi_i(t) \\
\varphi_i(t) &= -M^{1/2} V(X) \varphi_r(t),
\end{align*}
\]

which is the same as the Hamiltonian system (2.21)

\[
\begin{align*}
\dot{X}_t &= p_t \\
\dot{p}_t &= -\varphi_t \cdot \partial_X V(X_t) \phi_t \\
i \frac{M^{1/2}}{} \dot{\phi}_t &= V(X_t) \phi_t.
\end{align*}
\]

The Hamiltonian system yields a modified equation for the phase

\[
\dot{\tilde{\theta}} = \partial_X \tilde{\theta}_n \circ \dot{X} + \partial_{\varphi_r} \tilde{\theta}_n \cdot \dot{\varphi}_r = p \circ p + 2 \varphi_r \cdot V \varphi_r,
\]

since $\tilde{\theta} = \tilde{\theta}(X, \varphi_r)$ is a function of both $X$ and $\varphi_r$ in this formulation, and we see that $\tilde{\theta}$ is indeed a function of $X$, independent of $x$, so that the identification $\tilde{\theta} = \hat{\theta}$ is possible. The important property of this Hamiltonian dynamics is that $(X, p, \psi_n)$, with

\[
\dot{\psi}_n = \phi e^{iM^{1/2} \int_0^1 \phi \cdot V \phi(s) ds},
\]

solves both the Hamilton-Jacobi equation (2.18) and (2.17), written as the time-dependent Schrödinger equation (2.19).

The alternative (2.20) does not form a closed system, in the sense that the required function $\partial_X \psi_n(X_t)$ is not explicitly determined along the characteristics, but can be obtained from values of $\psi_n$, in a neighborhood of $X_t$, by differentiation.
2.5. Equations for the density. We note that
\[\psi_n = \left(\frac{\rho_n}{\dot{\psi}_n}\right)^{1/2}\psi_n,\]
\[\dot{\psi}_n = \left(\frac{\dot{\rho}_n}{\dot{\psi}_n}\right)^{1/2}\dot{\psi}_n,\]
shows that the densities \(\rho_n = \psi_n \cdot \psi_n\) and \(\dot{\rho}_n : = \dot{\psi}_n \cdot \dot{\psi}_n\), in addition to \((X,p,\tilde{\psi}_n)\) and \((\dot{X},\dot{\rho},\dot{\psi}_n)\), are needed to determine the wave functions \(\psi_n\) and \(\dot{\psi}_n\). Equation (2.17) and the projections in (2.3) subtracted (instead of added) imply that the approximate density \(\hat{\rho}_n\) satisfies
\[0 = \sum_j \int_{\mathbb{R}^3} (\partial_{X^j} \tilde{\psi}_n \dot{\psi}_n + \dot{\psi}_n \partial_{X^j} \tilde{\psi}_n) dx \partial_{X^j} \hat{\theta}_n + \int_{\mathbb{R}^3} \tilde{\psi}_n \dot{\psi}_n dx \partial_{X^j X^j} \hat{\theta}_n\]
\[= \sum_j \partial_{X^j} (\hat{\rho} \partial_{X^j} \hat{\theta}_n)\]
and consequently, the density can be determined along a characteristic using (2.7)
\[\dot{\hat{\rho}}(\dot{X}_t) = \sum_j \partial_{\dot{X}^j} \hat{\rho}(\dot{X}_t) \dot{\dot{X}}^j\]
\[= \sum_j \partial_{\dot{X}^j} \hat{\rho}(\dot{X}_t) \partial_{\dot{X}^j} \hat{\theta}_n\]
\[= -\hat{\rho}(\dot{X}_t) \sum_j \partial_{\dot{X}^j \dot{X}^j} \hat{\theta}_n\]
\[= -\hat{\rho}(\dot{X}_t) \text{ div } \hat{\rho}\]
\[= -\hat{\rho}(\dot{X}_t) \frac{d}{dt} \log |\hat{p}_t|\]
with the solution
\[\hat{\rho}(\dot{X}_t) = \frac{C}{|\hat{p}_t|},\]
where \(C\) is a positive constant for each characteristic. Change to coordinates \(\dot{X}_1 \in \mathbb{R}\) parallel and \(\dot{X}_0 \in \mathbb{R}^{3N-1}\) orthogonal to the characteristic direction \(\dot{X}\) to obtain the factorization
\[(2.23) \quad \hat{\rho}(\dot{X})d\dot{X} = \hat{\rho}(\dot{X}_0) \frac{d\dot{X}_0}{|\hat{p}_1|} \frac{d\dot{X}_1}{|\dot{\hat{p}}|} d\dot{t} = \hat{\rho}(\dot{X}_0) d\dot{X}_0 \frac{d\dot{t}}{T},\]
using
\[\frac{d\dot{X}_1}{|\dot{\hat{p}}|} = \frac{|d\dot{X}_1|}{|d\dot{X}_1/d\dot{t}|} = d\dot{t}\]
and the normalization
\[\int_{I \cap \mathbb{R}^{3(N+J)}} \hat{\rho}(\dot{X}_0) d\dot{X}_0 = 1.\]
Similarly, the exact Schrödinger density satisfies
\[
\dot{\rho}(X_t) = \sum_j \partial_{X_j} \rho(X_t) \dot{X}_j = -\rho(X_t) \frac{d}{dt} \log |p_t| + M^{-1/2} \sum_j \Im(\psi_n \cdot \Delta X_j \psi_n),
\]
where \(\Im w\) denotes the imaginary part of \(w\). Different characteristic paths \(\dot{X}_n(t) \in \mathbb{R}^{3N}\) have different densities. The density is therefore important to weight the different paths, in particular because the density in the time-independent case does not follow characteristics as in the time-dependent setting, which is explained in Section 4.2.

### 2.6. Construction of the solution operator

The WKB-form (2.1) is meaningful when \(\psi_n\) does not include the small scale, that is, we need to verify that \(\partial_X \psi_n\) is bounded independent of \(M\), which we do by using a spectral representation. In this section we present the set-up and the analysis is in Section 7. Section 7 also presents conditions so that \(\tilde{\psi}_n\) is \(O(M^{-1/2})\) close to an eigenvector of \(V\) in \(L^2(dx)\). To replace \(\tilde{\psi}_n\) by such an electron eigenstate is called the Born-Oppenheimer approximation, which has been studied for the time-independent [41, 7] and the time-dependent [24, 38] Schrödinger equations by different methods.

To construct the solution operator it is convenient to include a non interacting particle, i.e. a particle without charge, in the system and assume that this particle moves with constant high speed \(dX_1^1/\dot{t} = p_1^1 \gg 1\) (or equivalently with speed one and larger mass); such a non interacting particle does clearly not effect the other particles. The additional new coordinate \(X_1^1\) is helpful in order to simply relate the time-coordinate \(t\) and \(X_1^1\). To not change the original problem (1.1), add the corresponding kinetic energy \((p_1^1)^2/2\) to \(E\) and write equation (2.8) in the fast time scale \(\tau = M^{1/2}t\)

\[
i \frac{d}{d\tau} \tilde{\psi}_n = (V - V_n) \tilde{\psi}_n - \frac{1}{2M} G \sum_j \Delta X_j (G^{-1} \tilde{\psi}_n)
\]

and change to the coordinates

\[(\tau, X_0) := (\tau, X_1^1, X_2^1, X_3^1, X_2^2, \ldots, X_N) \in [0, \infty) \times I\]

instead of \((X^1, X^2, \ldots, X^N) \in \mathbb{R}^{3N}\), where \(X^j = (X_1^j, X_2^j, X_3^j) \in \mathbb{R}^3\), to obtain

\[
i \dot{\tilde{\psi}}_n + \frac{1}{2(p_1^1)^2} \tilde{\psi}_n = (V - V_n) \tilde{\psi}_n - \frac{1}{2M} G \sum_j \Delta X_0^j (G^{-1} \tilde{\psi}_n)
\]

\[
=: \tilde{V} \tilde{\psi}_n,
\]

using the notation \(\dot{w} = dw/d\tau\) in this section; note also that \(G\) is independent of \(X_1^1\). We see that the operator

\[
\tilde{V} := G^{-1} \tilde{V} G = G^{-1}(V - V_n) G - \frac{1}{2M} \sum_j \Delta X_0^j
\]
is Hermitian on \( L^2(\mathbb{R}^{3J+3N-1}) \). The solution of the eikonal equation (2.4), by the characteristics (2.5), becomes well defined in a domain \( U = [0, M^{1/2}t] \times \mathbb{R}^{3N-1} \), in the new coordinates. Assume now the data \((X_0, p_0, z_0)\) for \( X_0 \in \mathbb{R}^{3N-1} \) is \((L\mathbb{Z})^{3N-1}\)-periodic, then the also \((X_\tau, p_\tau, z_\tau)\) is \((L\mathbb{Z})^{3N-1}\)-periodic. To simplify the notation for such periodic functions, define the periodic circle \( \mathbb{T} := \mathbb{R}/(L\mathbb{Z}) \).

We seek a solution \( \Phi \) of (1.1) which is \((L\mathbb{Z})^{3(2J+3N-1)}\)-periodic in the \((x,X_0)\)-variable. The Schrödinger operator \( \bar{V}_\tau \) has, for each \( \tau \), real eigenvalues \( \{\lambda_m(\tau)\} \) with a complete set of eigenvectors \( \{p_m(x, X_0)\}_\tau \) orthogonal in the space of \( x \)-anti-symmetric functions in \( L^2(\mathbb{T}^{3J+3N-1}) \), see [4]; its proof uses that the operator \( \bar{V}_\tau + \gamma I \) generates a compact solution operator in the Hilbert space of \( x \)-anti-symmetric functions in \( L^2(\mathbb{T}^{3J+3N-1}) \), for the constant \( \gamma \in (0, \infty) \) chosen sufficiently large. The discrete spectrum and the compactness comes from Fredholm theory for compact operators and that the bilinear form \( \int_{\mathbb{T}^{3J+3N-1}} v \bar{V}_\tau w + \gamma vw \, dx \, dx_0 \) is continuous and coercive on \( H^1(\mathbb{T}^{3J+3N-1}) \), see [16] and Section 7.3. We see that \( \bar{V} \) has the same eigenvalues \( \{\lambda_m(\tau)\} \) and the eigenvectors \( \{G_\tau p_m(\tau)\} \), orthogonal in the weighted \( L^2 \)-scalar product

\[
v \cdot w := \int_{\mathbb{T}^{3N-1}} v \cdot w \, G^{-2} \, dx_0.
\]

The construction and analysis of the solution operator continues in Section 7 with the four steps spectral decomposition, derivatives of the wave function, discrete spectrum and the Born-Oppenheimer approximation.

**Remark 2.1** (Boundary conditions). The eigenvalue problem (1.1) makes sense not only in the periodic setting but also with alternative boundary conditions from interaction with an external environment, as seen from the minimization formulation. The inflow, with data given from the time-independent Schrödinger problem, and the outflow of characteristics gives a different perspective on molecular dynamics simulations and the possible initial data for the time-dependent Schrödinger equation.

3. **The time-dependent Schrödinger equation**

The corresponding time-dependent *Ansatz*

\[
\psi_n(x, X, t) e^{i M^{1/2}(\theta_n(x, t) + Et)}
\]

in the time-dependent Schrödinger equation [39]

\[
\frac{i}{M^{1/2}} \dot{\Phi} = H\Phi
\]

leads analogously to the equations

\[
\partial_t \theta_n + \frac{1}{2} \frac{\partial_x \theta_n}{|\partial_x \theta_n|^2} = E - V_n,
\]

\[
\partial_t \rho + \sum_j \partial_{X_j} (\rho \partial_{X_j} \theta_n) = M^{-1/2} \sum_j \Im(\psi_n \cdot \Delta_{X_j} \psi_n),
\]
coupled to the Schrödinger equation along its characteristics $X_t$

$$i \frac{M^{1/2}}{d} \frac{d}{dt} \tilde{\psi}_n(x, X_t, t) = (V - V_n) \tilde{\psi}_n - \frac{G}{2M} \sum_j \Delta X_j (\tilde{\psi}_n G^{-1}),$$

(3.2)

$$\dot{X}_n = -\frac{\partial X (\tilde{\psi}_n \cdot V \tilde{\psi}_n)}{\tilde{\psi}_n \cdot \tilde{\psi}_n},$$

with the same equation for $(X, p, \tilde{\psi}, \rho, z, \partial X p, \partial XX p)$ as for the characteristics (2.4) and (2.9) in the time-independent formulation. The Ehrenfest dynamics is therefore the same when derived from the time-dependent and time-independent Schrödinger equations and the additional coordinate, introduced by a non-interacting particle in the construction of the time-independent solution in Section 7, can be interpreted as time. A difference is that the time variable is given from the time-dependent Schrödinger equation and implies classical velocity, instead of the other way around for the time-independent formulation.

4. Surface-hopping and multiple states

In general the eigenvalue $E$ is degenerate with high multiplicity related to that several combinations of kinetic nuclei energy and potential energy sum to $E$

$$- \int_{\mathbb{T}^3(J+N)} \Phi^* (2M)^{-1} \sum_j \Delta X_j \Phi dx dX + \int_{\mathbb{T}^3(J+N)} \Phi^* V \Phi dx dX = E \int_{\mathbb{T}^3(J+N)} \Phi^* \Phi dx dX,$$

with different excitations of kinetic nuclei energy and Born-Oppenheimer electronic eigenstates. When several such states are excited, it is useful to consider a linear combination of eigenvectors $\sum_{n=1}^{\hat{n}} \psi_n e^{iM^{1/2} \theta_n} =: \Phi$, where the individual terms solve (1.1) for the same energy $E$. We have

(4.1)

$$H \Phi = E \Phi$$

and the normalization $\sum_{n=1}^{\hat{n}} \| \psi_n \|_{L^2}^2 = 1$ implies $\| \Phi \|_{L^2} = 1$. Such a solution $\Phi$ can be interpreted as an exact surface-hopping model. The usual surface-hopping models make a somewhat different Ansatz with the $x$-dependence of $\psi_n$ prescribed from a given orthonormal basis in $L(\mathbb{T}^3J)$ of wave functions of different energy and with explicit time-dependence, see [42, 41]. This section extends the Ehrenfest dynamics to multiple states and presents an example of hopping between characteristics in Ehrenfest dynamics.

4.1. Surface-hopping and Ehrenfest dynamics for multiple states. The characteristic $(X_n, p_n)$, the wave function $\tilde{\psi}_n$, the density $\rho_n$ and the phase $\theta_n(t) = \theta_n(x_t)$ determine the time-independent wave function $\psi_n$ and the corresponding Ehrenfest approximation

$$\sum_n \hat{\psi}_n (p_n \hat{\rho}_n)^{1/2} e^{iM^{1/2} \hat{\theta}_n} =: \Phi$$

(4.2)

$$\hat{\rho}_n(X) d\hat{X} = \hat{\rho}_n(X_0) dX_0 \frac{dt}{T}$$
yields an approximation to $\Phi$; the density of state $n$ is now a constant multiple, $r_n \geq 0$, of the one-state density $\hat{\rho}_n$ defined in (2.23), normalized to $\int_{T_{i(n+N)}} \hat{\rho}_n dX = 1$ and $\sum_{n=1}^n r_n = 1$. Note that by definition the Ehrenfest states $(\hat{X}_n, \hat{\psi}_n, \hat{\rho}_n)$, $n = 1, \ldots, n$, satisfying (2.19) and (2.23), are uncoupled.

As an alternative to the usual surface-hopping methods, simulating hopping between characteristics based on empirical hopping-rules, we propose to solve the Ehrenfest characteristics (2.23) for multiple states $n$ with (4.2) and then include the density weight in determining the outcome, in the usual probability sense of quantum mechanics, see Section 5.

4.2. Characteristics hopping in the Ehrenfest dynamics. Here we show that the Ehrenfest dynamics provides hopping between characteristic paths, within the same state $n$, due to varying velocity along the characteristic path. The density $\hat{\rho}_n$ does not in general move along the characteristic $\hat{X}_n$ as seen in the following simple example in the domain $\mathbb{R} \times [-1, 1] \ni (\hat{X}^1, \hat{X}^2)$

\[
\begin{align*}
\hat{X}^1 &= \hat{p}^1 = 0, \\
\hat{X}^2 &= \hat{p}^2(\hat{X}) = \begin{cases} 
(C + 2\epsilon^{-1}\hat{X}^2)^{1/2}, & \hat{X}^1 < 0 \\
(C - 2\epsilon^{-1}\hat{X}^2)^{1/2}, & \hat{X}^1 > 0,
\end{cases}
\end{align*}
\]

with vertical characteristics. This is a solution for the potential

\[
V(\hat{X}) = \begin{cases} 
\epsilon^{-1}\hat{X}^2 + C/2, & \hat{X}^1 < 0 \\
-\epsilon^{-1}\hat{X}^2 + C/2, & \hat{X}^1 > 0,
\end{cases}
\]

with a barrier at $\hat{X}^1 = 0$ and any constant $C \geq 2\epsilon^{-1}$. For the inflow-domain

$I := \{\hat{X}_0 := (\hat{X}^1, -1) \mid \hat{X}^1 \in \mathbb{R}\}$

the density becomes

\[
\hat{\rho}(\hat{X}) = \hat{\rho}(\hat{X}_0) \frac{1}{\int_{-1}^1 \hat{p}^2(d\hat{X}^2)}. 
\]

Choose the constant $C$ such that $\hat{p}^2(\hat{X}^1, -1) = \mu$, for $\hat{X}^1 < 0$, then $\hat{p}^2(\hat{X}^1, 1) = (\mu^2 + 4\epsilon^{-1})^{1/2}$, for $\hat{X}^1 < 0$. Take $\mu = \epsilon^{1/2}/2$ to have $(\mu^2 + 4\epsilon^{-1})^{1/2} \approx \mu^{-1}$. Choose also $\hat{p}^2(\hat{X}^1, -1) = (\mu^2 + 4\epsilon^{-1})^{1/2} \approx \mu^{-1}$, for $\hat{X}^1 > 0$, then $\hat{p}^2(\hat{X}^1, 1) = \mu$, for $\hat{X}^1 > 0$, so that the final density is the initial density reflected around $\hat{X}^1 = 0$, that is

$\hat{\rho}(\hat{X}^1, 1) = \hat{\rho}(-\hat{X}^1, -1)$.

For instance a particle almost concentrated near $\hat{X}^1 = -1$, initially at $\hat{X}^2 = -1$, becomes almost concentrated at $\hat{X}^1 = 1$, finally at $\hat{X}^2 = 1$; therefore the particle has crossed the barrier $\hat{X}^1 = 0$ without a particle path (i.e. a characteristic) crossing the barrier.

The corresponding continuity equation in the time-dependent setting, which has the same characteristics as the time-independent case, would need a boundary condition on its inflow

\[
\rho(\hat{X}) = \rho(\hat{X}_0) \frac{1}{\int_{-1}^1 \hat{p}^2(d\hat{X}^2)}. 
\]
domain $\mathbb{R} \times \{-1\} \times [0, T] \cup \mathbb{R} \times [-1, 1] \times \{0\}$ (instead of on $I = \mathbb{R} \times \{-1\}$) and therefore the setting is different from the time-independent.

5. Computation of observables

Assume the goal is to compute an observable

$$\int_{\mathbb{T}^{3N}} \Phi \cdot A\Phi dX$$

for a given bounded linear multiplication operator $A = A(X)$ on $L^2(\mathbb{T}^{3N})$ and a solution $\Phi$ of (4.1). We have

$$\int_{\mathbb{T}^{3N}} \Phi \cdot A\Phi dX = \sum_{n,m} \int_{\mathbb{T}^{3N}} A(\psi_n e^{iM^{1/2}\theta_n}) \cdot \psi_m e^{iM^{1/2}\theta_m} dX$$

(5.1)

$$= \sum_{n,m} \int_{\mathbb{T}^{3N}} A e^{iM^{1/2}(\theta_m - \theta_n)} (\psi_n \cdot \psi_m) dX.$$ 

We can chose the eigenfunctions $\{\psi_n e^{iM^{1/2}\theta_n} \mid n = 1, \ldots, \tilde{n}\}$, for the eigenvalue $E$ of (1.1), to be orthogonal in $L^2(\mathbb{T}^{(J+N)})$ by the Gram-Schmidt procedure, so that when $A$ is constant the integrals in the right hand side of (5.1) vanish for $n \neq m$. The integrand is oscillatory on the local scale $y \in \mathbb{R}^{3N}$, for $M^{1/2} \partial_X (\theta_n - \theta_m) \circ y \approx 1$, and assume the phase gradient satisfies

$$|\partial_X (\theta_n - \theta_m)| \geq c$$

for some positive constant $c$ and $n \neq m$. Then the integrals over $\mathbb{T}^{(J+N)}$ of such an oscillatory function $e^{iM^{1/2}(\theta_m - \theta_n)} \psi_n \cdot \psi_m$ with respect to a differentiable function $A$ is small of order $O(M^{-1/2})$:

$$\int_{\mathbb{T}^{3N}} h(X) e^{iM^{1/2}(\theta_m - \theta_n)} dX = -M^{-1/2} \int_{\mathbb{T}^{3N}} h(X) \sum_j \frac{i \partial_{X_j} (\theta_m - \theta_n)}{|\partial_X (\theta_m - \theta_n)|^2} \partial_{X_j} e^{iM^{1/2}(\theta_m - \theta_n)} dX$$

$$= -M^{-1/2} \int_{\mathbb{T}^{3N}} \sum_j \partial_{X_j} (h(X)) \frac{i \partial_{X_j} (\theta_m - \theta_n)}{|\partial_X (\theta_m - \theta_n)|^2} e^{iM^{1/2}(\theta_m - \theta_n)} dX$$

$$= O(M^{-1/2}).$$

Consequently we have

$$\int_{\mathbb{T}^{3N}} \Phi \cdot A\Phi dX = \sum_{n=1}^{\tilde{n}} \int_{\mathbb{T}^{3N}} A \psi_n \cdot \psi_n dX + O(M^{-1/2}),$$

(5.3)

in the case of multiple eigenstates, $\tilde{n} > 1$, and

$$\int_{\mathbb{T}^{3N}} \Phi \cdot A\Phi dX = \int_{\mathbb{T}^{3N}} A \psi_1 \cdot \psi_1 dX$$
for a single eigenstate. We will study the approximation

\[ \sum_{n} \int_{T} A \psi_{n} \cdot \psi_{n} dX = \sum_{n} \int_{T} A(X) \rho_{n}(X) dX \]

using the notation

\[ g(X_{n}, \tilde{\psi}_{n}, \rho_{n}) := A(X_{n}) \rho_{n}(X_{n}). \]

The factorization (2.23)

\[ \hat{\rho}(\hat{X}) d\hat{X} = \hat{\rho}(\hat{X}_{0}) \frac{dt}{T} = \hat{\rho}(\hat{X}_{0}) \frac{dt}{T} \]
implies that each term in the observable (5.4) can be determined by

\[ \int_{T} g(\hat{X}, \hat{\psi}_{n}, \hat{\rho}_{n}) d\hat{X} = \int_{0}^{T} \int_{I} A(\hat{X}_{t}) \hat{\rho}_{n}(\hat{X}_{0}) d\hat{X}_{0} \frac{dt}{T}. \]

To compute this integral requires to find an approximation \( \hat{\rho}_{n}(\hat{X}_{0}) \) of \( \rho_{n}(X_{0}) \), to replace the integrals by quadrature (with a finite number of characteristics \( \hat{X}_{j} \) and time steps), and to approximate the characteristics by the Ehrenfest solution \( (\hat{X}_{n}, \hat{\psi}_{n}) \)

\[ \int_{0}^{T} \int_{I} A(\hat{X}_{t}) \hat{\rho}_{n}(\hat{X}_{0}) d\hat{X}_{0} \frac{dt}{T} \simeq \sum_{\Delta t} \sum_{\Delta \hat{X}_{0}} A(\hat{X}_{t}) \hat{\rho}_{n}(\hat{X}_{0}) \Delta \hat{X}_{0} \Delta t. \]

The quadrature approximation is straightforward in theory, although costly in practical computations. Regarding the inflow density \( \hat{\rho}_{n} \mid _{I} \) there are two situations - either the characteristics return often to the inflow domain or not. If they do not return it is reasonable to define the inflow-density \( \hat{\rho}_{n} \mid _{I} \) as an initial condition. If characteristics return, the dynamics can be used to estimate the return-density \( \hat{\rho}_{n} \mid _{I} \) as follows: let \( \hat{X}' : [0, T] \to \mathbb{R}^{3N} \) denote Ehrenfest nuclei positions and assume that the following limits exist

\[ \lim_{M \to \infty} \lim_{T \to \infty} \frac{1}{MT} \int_{0}^{MT} A(\hat{X}_{t}) dt = \lim_{M \to \infty} \lim_{T \to \infty} \sum_{m=1}^{M} \frac{1}{mT} \int_{mT}^{(m+1)T} A(\hat{X}_{t}) dt \frac{dt}{T} \]

\[ = \lim_{T \to \infty} \int_{I} \int_{0}^{T} A(\hat{X}'_{t}) \frac{dt}{T} \hat{\rho}_{n}(\hat{X}'_{0}; \hat{X}_{0}) d\hat{X}'_{0}. \]

which bypasses the need to find \( \hat{\rho}_{n} \mid _{I} \) and the quadrature in the number of characteristics. A way to think about this limit is to sample the return points \( \hat{X}_{t} \in I \) and from these samples construct an empirical return-density, converging to \( \hat{\rho}_{n} \mid _{I} \) as the number of return iterations tends to infinity. We allow the density \( \hat{\rho}(\hat{X}'_{0}; \hat{X}_{0}) \) to depend on the initial position \( \hat{X}_{0} \); the more restrictive property to have \( \hat{\rho}(\hat{X}'_{0}; \hat{X}_{0}) \) constant as a function of \( \hat{X}_{0} \) is called ergodicity. If (5.6) holds we say that the dynamics is weakly ergodic. For the Ehrenfest Hamiltonian
dynamics (2.22), the possible densities generated by such weak ergodicity are limit solutions of the Liouville equation

\[
\partial_t \hat{\rho} + p \partial_X \hat{\rho} - \hat{\phi} \cdot \partial_X V \hat{\phi} \partial_p \hat{\rho} - M^{1/2} V \hat{\phi} \cdot \partial_{\phi} \hat{\phi} \hat{\rho} + M^{1/2} V \hat{\phi}_r \cdot \partial_{\phi} \hat{\phi} \hat{\rho} = 0,
\]

in the sense \( \hat{\rho} = \lim_{t \to \infty} \hat{\rho} \), which take the form \( \hat{\rho} = f(|p|^2/2 + \hat{\phi} \cdot V \hat{\phi}) \) for some functions \( f \) as described more in Section 6.3.

The more accurate density \( \rho_n(X) \) in (2.24) does not factorize as described more in Section 6.3.

\[ \rho(X)dX \neq \rho(X_0)dX_0dX_1^1/|p_1(X)| \]

and consequently ergodicity for the exact paths seems not hold in the same sense.

6. Approximation error derived from a Hamilton-Jacobi equation

A numerical computation of an approximation to \( \sum_n \int_{\mathbb{T}^1 \mathbb{N}} \psi_n \cdot A\psi_n dX \) has the main ingredients:

1. to approximate the exact characteristics by Ehrenfest characteristics (2.19),
2. to discretize the Ehrenfest characteristics equations, and either
3. if \( \rho|_I \) is an inflow-density, to introduce quadrature in the number of characteristics, or
4. if \( \rho|_I \) is a return-density, to replace the ensemble average by a time average using the weak ergodicity (5.6).

This section presents a derivation of the approximation error, avoiding the second discretization step studied for instance in [9, 10, 32].

6.1. The Ehrenfest approximation error. This section shows that both alternative Ehrenfest systems, written as a Hamiltonian system (1.5) or the alternative form (2.19), approximate Schrödinger observables. We see that the approximate wave function \( \hat{\Phi} \), defined by

\[
(6.1) \quad \hat{\Phi} = \hat{\rho}^{1/2} \hat{\psi}_n e^{iM^{1/2} \hat{\theta}_n},
\]

where \( \hat{\psi}_n = \hat{\phi}_n e^{iM^{1/2} \int_0^t \hat{\phi}_n V \hat{\phi}_n(s) ds} \) and \( (\hat{X}, \hat{\phi}_n) \) solves the Hamiltonian system (2.21) or the system (2.20), is an approximate solution to the Schrödinger equation (1.1)

\[
(6.2) \quad (H - E)\hat{\Phi} = -\frac{1}{2M} e^{iM^{1/2} \hat{\theta}_n} \sum_j \Delta_X \hat{\phi}_n(\hat{\rho}^{1/2} \hat{\psi}_n),
\]
since by (2.2), (2.9), (2.17) and (2.19)
\[
(H - E)\hat{\Phi} = - (iM^{-1/2}\hat{\psi}_n - (V - V_n)\hat{\psi}_n) \hat{\rho}^{1/2} e^{iM^{1/2}\hat{\theta}_n} \\
+ \left( \frac{|\partial_X\hat{\theta}_n|^2}{2} + \hat{\psi}_n \cdot V\hat{\psi}_n - E \right) \hat{\rho}^{1/2} \hat{\psi}_n e^{iM^{1/2}\hat{\theta}_n} \\
- \frac{e^{iM^{1/2}\hat{\theta}_n}}{2M} \sum_j \Delta_X j(\hat{\rho}^{1/2}\hat{\psi}_n) \\
= - \frac{1}{2M} e^{iM^{1/2}\hat{\theta}_n} \sum_j \Delta_X j(\hat{\rho}^{1/2}\hat{\psi}_n).
\]

Therefore \(\hat{\Phi}\) approximates a non degenerate eigenstate \(\Phi\), satisfying \(H\Phi = E\Phi\), or more generally the span of \(\hat{\Phi}\) approximates the eigenspace spanned by \(\Phi\). This section presents conditions for accurate approximation error of observables

\[
\int_{T^3N} g(X) \rho(X) dX - \int_{T^3N} g(X) \hat{\rho}(X) dX = \Phi \cdot \Phi - \hat{\Phi} \cdot \hat{\Phi}.
\]

The expansion in the orthonormal eigenpairs \(\{\lambda_n, \Phi_n\}\), satisfying \(H\Phi_n = \lambda_n\Phi_n\),

\[
\hat{\Phi} =: \sum_n \alpha_n \Phi_n
\]
yields

\[
\sum_n (\lambda_n - E)\alpha_n \Phi_n = - \frac{1}{2M} v,
\]

which establishes

\[
(\lambda_n - E)\alpha_n = - \frac{1}{2M} \int_{T^3N} \Phi_n \cdot v dX.
\]

Since \(\hat{\Phi}\) exists and solves (6.2), the right hand side satisfies

\[
\hat{\psi}_n = 0, \quad \text{for } n \text{ such that } \lambda_n = E.
\]

Use Parseval's relation to rewrite the \(L^2\)-norm of \(v\)

\[
\|v\|_{L^2(T^3J+N)}^2 = \sum_n |\hat{\psi}_n|^2
\]

We have \(\hat{\psi}_n = 0\), when \(\lambda_n = E\), and let

\[
|\hat{\psi}'_n(E)| := \lim_{\delta \to 0^+} \frac{|\hat{\psi}_n(E + \delta)|}{\delta},
\]
which implies
\[ \sum_n \frac{|\hat{v}_n(\lambda_n)|^2}{|\lambda_n - E|^2} \leq \sum_{\{n:|\lambda_n - E|<1\}} |\hat{v}_n'(E)|^2 + \sum_n |\hat{v}_n|^2. \]

Assume that
\[ \sum_n |\hat{v}_n|^2 = \mathcal{O}(1), \]
\[ \sum_{\{n:|\lambda_n - E|<1\}} |\hat{v}_n'(E)|^2 = \mathcal{O}(1). \]

Remark 6.2 motivates assumption (6.3), when the number of nuclei is large compared to \( M \). Assumption (6.3) yields
\[ 4M^2 \sum_{n: \lambda_n \neq E} |\alpha_n|^2 = \sum_n \frac{|\hat{v}_n|^2}{(\lambda_n - E)^2} = \mathcal{O}(1), \]
and we conclude that there exists an eigenstate \( \tilde{\Phi} \), satisfying \( H \tilde{\Phi} = E \tilde{\Phi} \), such that
\[ \| \tilde{\Phi} - \hat{\Phi} \|_{L^2(T^3(J+N))} = \mathcal{O}(M^{-1}). \]

Let \( \rho := \tilde{\Phi} \cdot \hat{\Phi} \) and \( \hat{\rho} := \hat{\Phi} \cdot \hat{\Phi} \). We have
\[ \text{Theorem 6.1. Assume that the bound (6.4) holds, then Ehrenfest dynamics (6.1) approximates Schrödinger observables with the error bounded by } \mathcal{O}(M^{-1}) : \]
\[ \int_{T^3N} g(\hat{X})\hat{\rho}(\hat{X})d\hat{X} = \int_{T^3N} g(X)\rho(X)dX + \mathcal{O}(M^{-1}). \]

This derivation assumed that \( v = e^{iM t/2} \sum_j \Delta_X (\hat{\rho}^{1/2} \hat{\psi}) \) is bounded in \( L^2(T^3(J+N)) \) and used the residual, \( v/(2M) \), of the Ehrenfest solution \( (\hat{X}, \hat{p}, \hat{\psi}_n) \) inserted into the time-independent Schrödinger equation (1.1) with the solution \( \hat{\Phi} \); the derivation did not use the exact solution paths \( (X,p,\psi_n) \) obtained from the exact characteristics. The observable may include the time variable, through the position of a non interacting (non-charged) nucleon moving with given velocity, so that transport properties as e.g. the diffusion and viscosity of a liquid may by determined, cf. [21].

\[ \text{Remark 6.2. So far we did not use that the system size is large; to motivate assumption (6.3) we will use that the number of nuclei } N \text{ is large compared to } M, \text{ so that } M/N \text{ is negligible small. We have } \partial_{\lambda_n} \hat{v}_n = \int_{T^3N} \partial_{\lambda_n} \Phi_n \cdot vdX \text{ and to estimate the derivative } \partial_{\lambda_n} \Phi_n \text{ we make a perturbation } \delta \text{ of the total energy } \lambda_n \text{ and study its effect on the eigenfunction } \Phi_n. \]

When \( \lambda_n = |p|^2/2 + V_n \) is perturbed by \( \delta \), we assume that this energy \( \delta \) is spread approximately uniformly to all nuclei as kinetic energy, so that the momentum for each particle changes only \( \mathcal{O}(\delta N^{-1}) \). The assumption that the perturbation energy is spread to kinetic energy uniformly comes with a question, why uniformly and not, for instance, all energy to one particle: we know there are many eigenstates with eigenvalue \( \lambda_n + \delta \) and we pick one special that is close to \( \Phi_n \) by making this almost uniform distribution of kinetic energy. Then the particle paths
change negligible and the eigenvector $\Phi = \psi e^{iM^{1/2}\theta}$ has almost the same path $(X, p, \psi)$. The phase, written as

$$\theta = 2 \int_0^t \lambda_n - V_n ds,$$

can also have negligible change by considering the perturbed phase at time $t'$, depending on the change from $\lambda_n$ to $\lambda_n + \delta$ through

$$\int_0^{t'} \lambda_n + \delta - V_n ds = \int_0^t \lambda_n - V_n ds,$$

so that the phase $\theta$ does not change. We see that for large $N$ the derivative $\partial_{\lambda_n} \Phi_n$ becomes negligible small and hence $\partial_{\lambda_n} \hat{\psi}_n = \int_{\mathbb{T}^N} \partial_{\lambda_n} \Phi_n \cdot v dX$ is small. Section 7.2 motivates the $L^2$-bound $\|v\|_{L^2} = \sum_n |\hat{\psi}_n|^2 = O(1)$, from derivatives of the electron wave function, using a spectral decomposition in $L^2(dx dX)$.

6.2. **The Born-Oppenheimer approximation.** The Born-Oppenheimer approximation leads to the standard formulation of *ab initio* molecular dynamics, in the micro-canonical ensemble with constant number of particles, volume and energy, for the nuclei positions $\bar{X}$,

$$\dot{\bar{X}} = -\partial_X V_0$$

$$V_0 := \frac{\psi_0 \cdot V \psi_0}{\psi_0 \cdot \psi_0},$$

by using that the electrons are in the eigenstate $\psi_0$ with eigenvalue $V_0$ to $V$. The Born-Oppenheimer dynamics approximates the Ehrenfest dynamics

$$\ddot{\hat{\psi}} = -\hat{\psi}_n \cdot \partial_X \hat{V} \hat{\psi}_n.$$ 

In (7.14) we show that $\hat{\psi}_n = \psi_0 + O(M^{-1/2})$, which yields $O(M^{-1/2})$ difference between the two right hand sides. A more careful study of such approximations with stochastic initial data for $\hat{\psi}_n - \psi_0$, depending on the temperature, is in Section 6.3. Here we apply the error analysis of the previous section to the Born-Oppenheimer approximation.

The Born-Oppenheimer approximation can be analyzed similarly as the Ehrenfest dynamics by using the approximation

$$\hat{\Phi} = \hat{\rho}^{1/2} \psi_0 e^{iM^{1/2}\hat{\theta}_0},$$

satisfying

$$(H - E)\hat{\Phi} = -M^{-1/2} \hat{\psi}_0 \hat{\rho}^{-1/2} - \frac{1}{2M} e^{iM^{1/2}\hat{\theta}_0} \sum_j \Delta_X (\hat{\rho}^{1/2} \psi_0),$$

with the additional residual term including the bounded factor $\hat{\psi}_0 = \partial_X \psi_0 \circ \hat{X} = O(1)$. Apply the derivation in the previous section to deduce
Theorem 6.3. Assume that \( v = e^{it\hat{H}}(i\psi_0\hat{\rho}^{1/2} - (2M)^{-1/2}\sum_j \Delta_{X_j}(\hat{\rho}^{1/2}\psi_0)) \in L^2(T^{3(j+N)}) \) and suppose that (6.4) holds for this \( v \), then the Born-Oppenheimer dynamics (6.6) approximates, in the weakly ergodic case (5.6), Schrödinger observables with error bounded by \( O(M^{-1/2}) \):

\[
\lim_{T \to \infty} \int_0^T g(\bar{X}_t) \frac{dt}{T} = \int_{T^{3N}} g(X)\bar{\rho}(X)dX = \int_{T^{3N}} g(X)\rho(X)dX + O(M^{-1/2}).
\]  

(6.8)  

6.3. Stochastic Langevin and Smoluchowski molecular dynamics approximation.  
In this section we analyze a situation when the electron wave function in the Ehrenfest dynamics is perturbed from its ground state by thermal fluctuations, which will lead to molecular dynamics in the canonical ensemble with constant number of particles, volume and temperature. To determine the stochastic data for \( \phi \) requires some additional assumptions. Inspired by the study of a classical heat bath of harmonic oscillators in [44], we will sample the initial data for \( \phi \) randomly from a probability density given by an equilibrium solution \( f \) (satisfying \( \partial_t f = 0 \)) of the Liouville equation \( \partial_t f + \partial_{\rho E} H_E \partial_{r E} f - \partial_{r E} H_E \partial_{\rho E} f = 0 \), to the Ehrenfest dynamics (2.22). There are many such equilibrium solutions, e.g. \( f = h(H_E) \) for any differentiable function \( h \) and there may be equilibrium densities that are not functions of the Hamiltonian. As mentioned in Section 5, the set of densities \( \bar{\rho} \), corresponding to the different eigenstates, forms the relevant set of equilibrium solutions.

To find the equilibrium solution to sample \( \phi \) from, we may first consider the marginal equilibrium distribution for the nuclei in the Ehrenfest Hamiltonian system. The equilibrium distribution of the nuclei is simpler to understand than the equilibrium of electrons: in a statistical mechanics view, the marginal probability of finding the now classical nuclei with the energy \( H_E := 2^{-1}|\rho|^2 + \phi \cdot V(X)\phi \) (for given \( \phi \)) is proportional to the Gibbs-Boltzmann factor \( \exp(-H_E/T) \), where the positive parameter \( T \) is the temperature, in units of the Boltzmann constant, cf. [17], [27]. Assuming that equilibrium density is a function of the Hamiltonian, its marginal distribution therefore satisfies

\[
\int h(2^{-1}|\rho|^2 + \phi \cdot V(X)\phi) d\phi_i d\phi_j = e^{-|\rho|^2/(2T)} C(X)
\]

for some function \( C : \mathbb{R}^{3N} \to \mathbb{R} \) and Fourier transformation with respect to \( |\rho| \in \mathbb{R} \) of this equation implies the Gibbs distribution \( h(H_E) = ce^{-H_E/T} \), for a normalizing constant \( c = 1/\int \exp(-H_E/T)d\phi_i d\phi_j dX dp \). In this perspective the nuclei act as the heat bath for the electrons. The work [28] considers Hamiltonian systems where the equilibrium densities are assumed to be a function of the Hamiltonian and shows that the first and second law of (reversible) thermodynamics hold (for all Hamiltonians depending on a multidimensional set of parameters) if and only if the density is the Gibbs exponential \( \exp(-H_E/T) \) (the ”if” part was formulated already by Gibbs [23]); in this sense, the Gibbs
distribution is more stable than other equilibrium solutions. An alternative motivation of the
Gibbs distribution, based on the conclusion of this work (in a somewhat circular argument),
is that the nuclei can be approximated by classical Langevin dynamics with the unique invar-
iant density \( \exp \left( -\frac{|p|^2}{2} - \lambda_0(X) \right) / T \), which is an accurate approximation of the marginal
distribution of \( \exp(-H_E/T) \) when integrating over all the electron states \( \phi \), see Lemma 6.4
and Theorem 6.6. Note that there is only one function of the Hamiltonian where the momenta
\( p_j \) are independent and that is when \( f(r_E, p_E) \) is proportional to \( \exp \left( -\frac{H_E}{T} \right) \).

Since the energy is conserved for the Ehrenfest dynamics –now viewed with the electrons
as the primary systems coupled to the heat bath of nuclei– the probability of finding the electrons
in a certain configuration \( \phi \) is the same as finding the nuclei in a state with energy \( H_E \), which is
proportional to \( \exp(-H_E/T) \) in the canonical ensemble. This conclusion, that the probability
to have an electron wave function \( \phi \) is proportional to \( \exp \left( -\frac{H_E}{T} \right) \) \( d\phi \)
denotes our motivation to
sample the data for \( \phi \) from the conditioned density generated be \( \exp \left( -\frac{\phi \cdot V(x) \phi}{T} \right) \),
since we seek data for the electrons, we use the probability distribution for \( \phi \) conditioned on
\((X,p)\).

We compare in Remark 6.5 our model of initial data with a more standard model of initial
data, having given probabilities to be in mixed states, which is not an equilibrium solution
of the Ehrenfest dynamics. To sample from the Gibbs equilibrium density is standard in
classical Hamiltonian statistical mechanics but it seems non standard for Ehrenfest quantum
dynamics.

6.3.1. The Constrained Stochastic Initial Data. As in models of heat baths [19, 18] and [44] we
assume that the initial data of the light particles (here the electrons) are stochastic, sampled
from an equilibrium distribution of the Liouville equation. All states in this distribution
correspond to pure eigenstates of the full Schrödinger operator with energy \( E \). There are
many such states and here we use the canonical ensemble where the data is in state \( \phi \) with
the Gibbs-Boltzmann distribution proportional to \( \exp \left( -\frac{H_E}{T} \right) d\phi \), i.e. in any state
\( \phi \), for \( \|\phi\| = 1 \), with probability weight
\[
\frac{e^{-\phi \cdot V(x/\phi)} d\phi d\phi^\dagger}{\int_{R^{2\times 1}} e^{-\phi \cdot V(x/\phi)} d\phi d\phi^\dagger}.
\]

Let us now determine precise properties of this distribution generated by the Hamiltonian
\( H_E \). To reduce the complication of the constraint \( \phi \cdot \phi = 1 \), we change variables \( \phi = \tilde{\phi} / \phi \cdot \tilde{\phi} \)
and write the Hamiltonian equilibrium density as
\[
\exp \left( -\left( p \cdot p / 2 + \lambda_0 + \frac{\tilde{\phi} \cdot (V - \lambda_0) \tilde{\phi}}{\phi \cdot \tilde{\phi}} \right) / T \right) d\tilde{\phi} d\phi d\phi^\dagger dX.
\]

Diagonalize the electron operator \( V(X^t) \) by the normalized eigenvectors and eigenvalues
\( \{\tilde{p}_j, \lambda_j\} \)
\[
\tilde{\phi} \cdot V(X^t) \tilde{\phi} = \lambda_0 + \sum_{j>0} (\lambda_j - \lambda_0) |\gamma_j|^2
\]
where

\[ \tilde{\phi} = \sum_{j \geq 0} \gamma_j \tilde{p}_j, \]

\[ (V - \lambda_0) \tilde{p}_j = \tilde{\lambda}_j \tilde{p}_j, \]

\[ \tilde{\lambda}_0 = 0, \]

with real and imaginary parts \( \gamma_j =: \gamma_j^r + i \gamma_j^i \). The orthogonal transformation \( \tilde{\phi} = \sum_j \gamma_j \tilde{p}_j \) shows that the probability density (6.9) is given by

\[ (6.10) \quad D := \frac{\left( \prod_{j > 0} e^{-\tilde{\lambda}_j |\gamma_j|^2/(T \sum_{j \geq 0} |\gamma_j|^2)} d\gamma_j^r d\gamma_j^i \right) e^{-(p_{\text{pop}}/2 + \lambda_0(X))/T} d \lambda d X}{\int_{\mathbb{R}^N} \left( \prod_{j > 0} \int_{\mathbb{R}^2} e^{-\tilde{\lambda}_j |\gamma_j|^2/(T \sum_{j \geq 0} |\gamma_j|^2)} d\gamma_j^r d\gamma_j^i \right) e^{-(p_{\text{pop}}/2 + \lambda_0(X))/T} d \lambda d X}, \]

using that the determinant of the matrix of eigenvectors is one.

If we neglect the constraint and set \( \sum_{j \geq 0} |\gamma_j|^2 = 1 \) the joint distribution density \( D \) simplifies to

\[ \frac{\left( \prod_{j > 0} e^{-\tilde{\lambda}_j |\gamma_j|^2/T} d\gamma_j^r d\gamma_j^i \right) e^{-(p_{\text{pop}}/2 + \lambda_0(X))/T} d \lambda d X}{\int_{\mathbb{R}^N} \left( \prod_{j > 0} \int_{\mathbb{R}^2} e^{-\tilde{\lambda}_j |\gamma_j|^2/T} d\gamma_j^r d\gamma_j^i \right) e^{-(p_{\text{pop}}/2 + \lambda_0(X))/T} d \lambda d X}, \]

where \( \{ \gamma^r_j, \gamma^i_j, j > 0 \} \) are independent and each \( \gamma_j^r \) and \( \gamma_j^i \) is normally distributed with mean zero and variance \( T/\tilde{\lambda}_j \). We see in Lemma 6.4 that this approximation is accurate, provided the spectral gap conditions

\[ \frac{T}{\tilde{\lambda}_1} \ll 1 \]

\[ (6.11) \min_{X_c \in Q} \max_{X \in Q} \left| \sum_{j > 0} \frac{\partial_X \tilde{\lambda}_j(Y) \circ (X - X_c)}{\tilde{\lambda}_j(Y)} \right| =: \alpha \ll 1 \]

holds, where \( Q \) is the set of attained nuclei positions.

**Lemma 6.4.** Assume the electron eigenvalues have a spectral gap around the ground state eigenvalue \( \lambda_0 \), in the sense that (6.11) holds. Then the marginal probability mass

\[ r(X) := \prod_{j \geq 0} \int_{|\gamma_j|^2 < C} e^{-\tilde{\lambda}_j |\gamma_j|^2/(T \sum_{j \geq 0} |\gamma_j|^2)} d\gamma_j^r d\gamma_j^i \]

satisfies

\[ (6.12) \quad |\log \frac{r(X)}{r(X_c)}| \leq \alpha \]
Proof. We first note that \( \|\hat{\phi}\|_{L^2} \) is bounded so that each component \( |\gamma_j| \) is also bounded. Each integral factor has the derivative

\[
\partial_X \int_{|\gamma_n|^2 < C} e^{-\lambda_n|\gamma_n|^2/(T \sum_{j \geq 0} |\gamma_j|^2)} d\gamma_n^r d\gamma_n^i = \frac{\partial_X \lambda_n(X)}{\lambda_n(X)} \int_{|\gamma_n|^2 < C} \frac{\lambda_n|\gamma_n|^2}{T \sum_{j \geq 0} |\gamma_j|^2} e^{-\lambda_n|\gamma_n|^2/(T \sum_{j \geq 0} |\gamma_j|^2)} d\gamma_n^r d\gamma_n^i
\]

for \( n \neq 0 \) and the derivative equal to zero for \( n = 0 \), so that

\[
\partial_X r(X) = r(X) \sum_{n > 0} \frac{\partial_X \lambda_n(X)}{\lambda_n(X)} \int_{|\gamma_n|^2 < C} \frac{\lambda_n|\gamma_n|^2}{T \sum_{j \geq 0} |\gamma_j|^2} e^{-\lambda_n|\gamma_n|^2/(T \sum_{j \geq 0} |\gamma_j|^2)} d\gamma_n^r d\gamma_n^i.
\]

The integral in the denominator has the estimate

\[
\int_{|\gamma_n|^2 < C} e^{-\lambda_n|\gamma_n|^2/(T \sum_{j \geq 0} |\gamma_j|^2)} d\gamma_n^r d\gamma_n^i = \frac{T}{\lambda_n} \sum_{j \neq n} |\gamma_j|^2 \int_{|\gamma_n|^2 < C} e^{-|\gamma_n|^2/(1+\lambda_n^{-1}T)|\gamma_n|^2} d\gamma_n^r d\gamma_n^i
\]

\[
= \frac{T}{\lambda_n} \sum_{j \neq n} |\gamma_j|^2 \int_{|\gamma_n|^2 < \epsilon \lambda_n/T} e^{-\gamma_n|^2/(1+\lambda_n^{-1}T)|\gamma_n|^2} d\gamma_n^r d\gamma_n^i + \mathcal{O}(\lambda_n T^{-1} e^{-\lambda_n \epsilon/(2T)}).
\]

where

\[
\int_{|\gamma_n|^2 < \epsilon \lambda_n/T} e^{-|\gamma_n|^2} d\gamma_n^r d\gamma_n^i \leq \int_{|\gamma_n|^2 < \epsilon \lambda_n/T} e^{-|\gamma_n|^2/(1+\lambda_n^{-1}T)|\gamma_n|^2} d\gamma_n^r d\gamma_n^i
\]

\[
\leq (1 + \epsilon) \int_{|\gamma_n|^2 < \epsilon \lambda_n/(T(1+\epsilon))} e^{-|\gamma_n|^2} d\gamma_n^r d\gamma_n^i.
\]

Choose \( \epsilon = 4T \lambda_n^{-1} \log(\lambda_n/T) \) to obtain

\[
\int_{|\gamma_n|^2 < C} e^{-\lambda_n|\gamma_n|^2/(T \sum_{j \geq 0} |\gamma_j|^2)} d\gamma_n^r d\gamma_n^i = \frac{T}{\lambda_n} \sum_{j \neq n} |\gamma_j|^2 \left( \pi + \mathcal{O}(T \lambda_n^{-1} \log(\lambda_n T^{-1})) \right).
\]

We have similarly

\[
\int_{|\gamma_n|^2 < C} \frac{\lambda_n|\gamma_n|^2}{T \sum_{j \geq 0} |\gamma_j|^2} e^{-\lambda_n|\gamma_n|^2/(T \sum_{j \geq 0} |\gamma_j|^2)} d\gamma_n^r d\gamma_n^i
\]

\[
= \frac{T}{\lambda_n} \sum_{j \neq n} |\gamma_j|^2 \left( \frac{\pi}{2} + \mathcal{O}(T \lambda_n^{-1} \log(\lambda_n T^{-1})) \right),
\]

which implies that

\[
| \log \frac{r(X)}{r(X_c)} | = \left| \int_0^1 \frac{\partial_X r}{r} (sX_c + (1-s)X) o (X - X_c) ds \right| \leq \alpha.
\]
Remark 6.5. Entropy and the Standard Canonical Density Distribution. Let $q_j := |\gamma_j|^2$ denote the density of state $j$ in the initial data $\phi_0$. In the usual setting of a canonical distribution

\[(6.13) \quad q_j = e^{-\bar{\lambda}_j/T} / \sum_j e^{-\bar{\lambda}_j/T},\]

which follows from maximizing the von Neumann entropy defined by $-\sum_j q_j \log q_j$, with the probability and energy constraints $\sum_j q_j = 1$ and $\sum_j \bar{\lambda}_j q_j = \text{constant}$, see [22]. The almost chi-square distribution (6.10) of $\bar{\lambda}_j q_j / T = \bar{\lambda}_j |\gamma_j|^2 / T$ is clearly different from that; its motivation in Sections 6.3 and 6.3.1 as the equilibrium solution $\exp(-\tilde{H}_E/T)$ of the Liouville equation for the Ehrenfest Hamiltonian dynamics, viewed as a system of electrons coupled to a heat bath of classical nuclei – seems more fundamental to me, since the canonical distribution (6.13) is not an equilibrium density of the Ehrenfest dynamics.

6.3.2. The stochastic molecular dynamics models. In this subsection we consider the special case when the observable does not depend on the time variable (and the velocity). Then it is enough to determine an integral with respect to the invariant measure; there are several alternatives, cf. [9], and we focus on ensemble averages computed by stochastic Langevin and Smoluchowski dynamics. The observable in the Ehrenfest dynamics is

\[
\int_{\mathbb{R}^{3N}} g(X) e^{-\lambda_0(X)/T} r(X) dX / \int_{\mathbb{R}^{3N}} e^{-\lambda_0(X)/T} r(X) dX = \int_{\mathbb{R}^{3N}} g(X) e^{-\lambda_0(X)/T} r(X) dX / \int_{\mathbb{R}^{3N}} e^{-\lambda_0(X)/T} r(X) dX + \log \frac{r(X)}{r(X_c)} dX
\]

where by Lemma 6.4

\[
\frac{T}{|\lambda_0|} \log \frac{r(X)}{r(X_c)} = O(T|\lambda_0|^{-1}\alpha),
\]

which implies

\[(6.14) \quad \frac{\int_{\mathbb{R}^{3N}} g(X) e^{-\lambda_0(X)/T} r(X) dX}{\int_{\mathbb{R}^{3N}} e^{-\lambda_0(X)/T} r(X) dX} = \frac{\int_{\mathbb{R}^{3N}} g(X) e^{-\lambda_0(X)/T} dX}{\int_{\mathbb{R}^{3N}} e^{-\lambda_0(X)/T} dX} + O(T|\lambda_0|^{-1}\alpha).\]

Let $W_t$ denote the standard Brownian process (at time $t$) in $\mathbb{R}^{3N}$ with independent components and let $K$ be a positive parameter. The stochastic Langevin dynamics

\[
dX_t = p_t dt
\]

\[
dp_t = -\partial_X \lambda_0(X_t) dt - Kp_t dt + \sqrt{2TK} dW_t
\]

and the Smoluchowski dynamics

\[
dX_s = -\partial_X \lambda_0(X_s) ds + \sqrt{2T} dW_s
\]
has the unique invariant probability density
\[ e^{-(p \cdot p/2 + \lambda_0(X)) / T} d\rho dX \]
respectively
\[ e^{-\lambda_0(X) / T} dX \]
\[ \int_{\mathbb{R}^N} e^{-\lambda_0(X) / T} dX, \]
cf. [9]. The hydrogen atom has eigenfunctions with a singularity proportional to \( e^{-\beta|x|} \) for some positive constant \( \beta \). Also in the case of many electrons and one nuclei located at \( X_1 \in \mathbb{R}^3 \), the electron eigenfunction \( \bar{\rho}_n \) are Lipschitz continuous and have a singularity proportional to \( |x_j - X_1| \), see [20]; such eigenfunctions \( \psi \) have bounded \( \|\Delta_X \psi\|_{L^2} \) norm. If we still assume that our Ehrenfest solution satisfies the bound (6.3) and that its density is \( \hat{\rho} = e^{-H_E / T} \) the combination of (6.14) and Theorem 6.1 imply

**Theorem 6.6.** Both the Langevin and Smoluchowski stochastic molecular dynamics approximate Schrödinger observables with error bounded by \( O(M^{-1} + T|\lambda_0|^{-1}\alpha) \), provided the assumption in Theorem 6.1 holds together with the spectral gap condition (6.11).

The ground state energy \( \lambda_0 \) is an extensive variable with its value proportional to the number of particles \( N + J \), as follows from stability of bulk matter [34]. The error term \( T\alpha\lambda_0^{-1} \) will then be small if \( |\partial_X \lambda_j \circ (X - X_c)| \) is small for \( j > J_0 \), with \( J_0 \ll N + J \), resembling free electron eigenvalues for a constant potential.

6.3.3. **Brownian Particles in a Heat Bath.** The particles with coordinates \( x \), in (1.5), can also be interpreted as a heat bath of lighter particles consisting of both nuclei and electrons, i.e. not necessarily only of electrons, so that the Langevin equation (1.6) and the Smoluchowski equation (1.7) also describe approximately the dynamics \( X \) of heavy so called Brownian particles. This subsection presents some background on deriving the Langevin equation for heavy particles in a heat bath.

Theorem 6.6 is relevant for the central problem in statistical mechanics to show that Hamiltonian dynamics of heavy particles, coupled to a heat bath of many lighter particles with random initial data, can be approximately described by Langevin’s equation, as motivated by the pioneering work [15],[31] and continued with more precise heat bath models, based on harmonic interactions, in [19, 18] [44]. More recently these models of a heavy, so called Brownian, particle coupled to a heat bath are also used for numerical analysis studies related to coarse-graining in molecular dynamics and weak convergence analysis [40, 30] [25], for strong convergence analysis [1], and for computational studies on nonlinear heat bath models [11, 29]. Langevin’s equation has also been derived from a heavy particle colliding with an ideal gas heat bath, where the initial light particle positions are modeled by a Poisson point process and initial particle velocities are independent Maxwell distributed; the heavy particle collides elastically with the ideal gas particles and moves uniformly in between, see [14, 13].

An important inspiration for this work is [44], where Zwanzig derives a generalized Langevin equation for a (Brownian) particle coupled to a heat bath particle system through a harmonic
interaction potential with \textit{ad hoc} prescribed heat bath frequency distribution and coupling; similar assumptions on deterministic or stochastic frequency distributions and coupling are used in the above cited references. This work extends the ideas in \cite{44} by using the \textit{ab initio} Ehrenfest dynamics (1.5) for nuclei and electrons, or (1.5) for heavy nuclei coupled to a heat bath of lighter nuclei and all electrons modeled by a Schrödinger equation. Another difference is that the heavy nuclear mass is here used to find a proper Langevin equation avoiding the integral coupling in the generalized Langevin equation. On the other hand, our analysis leaves the friction parameter $K$ undetermined.

7. Construction of the solution operator

This section continues the construction of the solution operator started in Section 2.6. Assume for a moment that $\tilde{V}$ is independent of $\tau$. Then the solution to (2.8) can be written as a linear combination of the two exponentials

$$Ae^{i\alpha_+} + Be^{i\alpha_-}$$

where

$$\alpha_\pm = (p_1^i)^2 \left(-1 \pm (1 - 2(p_1^i)^{-2}\tilde{V})^{1/2}\right).$$

We see that $e^{i\alpha_-}$ is a highly oscillatory solution on the fast $\tau$-scale with

$$\alpha_- = -2(p_1^i)^2 + \tilde{V} + \mathcal{O}(\tilde{V}^2/(p_1^i)^2),$$

while

$$(7.1) \quad \alpha_+ = -\tilde{V} + \mathcal{O}(\tilde{V}^2/(p_1^i)^2).$$

Therefore we chose initial data

$$i\dot{\tilde{\psi}}_n|_{\tau=0} = -\alpha_+ \tilde{\psi}_n|_{\tau=0}$$

to have $B = 0$, which eliminates the fast scale, and the limit $p_1^i \to \infty$ determines the solution by the Schrödinger equation

$$i\dot{\tilde{\psi}}_n = \tilde{V}\tilde{\psi}_n.$$

The next section presents an analogous construction for the slowly, in $\tau$, varying operator $\tilde{V}$.

7.1. Spectral decomposition. Write (2.25) as the first order system

$$i\dot{\tilde{\psi}}_n = v$$

$$\dot{v} = 2(p_1^i)^2 i(\tilde{V}\tilde{\psi}_n - v)$$

which for $\tilde{\psi} := (\tilde{\psi}_n, v)$ takes the form

$$\dot{\tilde{\psi}} = iA\tilde{\psi} \quad A := \begin{pmatrix} 0 & -1 \\ 2(p_1^i)^2\tilde{V} & -2(p_1^i)^2 \end{pmatrix},$$
where the eigenvalues $\lambda_\pm$, right eigenvectors $q_\pm$ and left eigenvectors $q^{-1}_\pm$ of the real matrix $A$ are

$$\lambda_\pm := (p_1^1)^2 \left( -1 \pm \left( 1 - 2(p_1^1)^{-2}\tilde{V} \right)^{1/2} \right),$$

$$q_+ := \begin{pmatrix} 1 \\ -\lambda_+ \end{pmatrix},$$

$$q_- := \begin{pmatrix} -\lambda_-^{-1} \\ 1 \end{pmatrix},$$

$$q^{-1}_+ := \frac{1}{1 - \lambda_+/\lambda_-} \begin{pmatrix} 1 \\ \lambda_-^{-1} \end{pmatrix},$$

$$q^{-1}_- := \frac{1}{1 - \lambda_+/\lambda_-} \begin{pmatrix} \lambda_+ \\ 1 \end{pmatrix}.$$ 

We see that $\lambda_+ = -\tilde{V} + \mathcal{O}(\tilde{V}^2(p_1^1)^{-2})$ and $\lambda_- = -2(p_1^1)^2 + \tilde{V} + \mathcal{O}(\tilde{V}^2(p_1^1)^{-2})$. The important property here is that the left eigenvector $\lim_{p_1^1 \to \infty} q^{-1}_+ = (1, 0)$ is constant, independent of $\tau$, which implies that the $q_+$ component $q^{-1}_+ \tilde{\psi} = \tilde{\psi}_n$ decouples: we obtain in the limit $p_1^1 \to \infty$ the time-dependent Schrödinger equation

$$i \dot{\tilde{\psi}}_n(\tau) = i \frac{d}{d\tau} (q^{-1}_+ \tilde{\psi}_\tau)$$

$$= iq^{-1}_+ \frac{d}{d\tau} \tilde{\psi}_\tau$$

$$= -q^{-1}_+ A_\tau \tilde{\psi}_\tau$$

$$= -\lambda_+(\tau)q^{-1}_+ \tilde{\psi}_\tau$$

$$= -\lambda_+(\tau) \tilde{\psi}_n(\tau)$$

$$= \tilde{V}_\tau \tilde{\psi}_n(\tau)$$

where the operator $\tilde{V}_\tau$ depends on $\tau$ and $(x, X_0)$. Define the solution operator $S$

$$\tilde{\psi}_n(\tau) = S_{t,0} \tilde{\psi}_n(0).$$

The operator $\tilde{V}$ can be symmetrized

$$\tilde{V}_\tau := G^{-1}_\tau \tilde{V}_\tau G = (V - V_n)_\tau - \frac{1}{2M} \sum_j \Delta x_j^3,$$

with real eigenvalues $\{\lambda_m\}$ and orthonormal eigenvectors $\{p_m\}$, satisfying

$$\tilde{V}_\tau p_m(\tau) = \lambda_m(\tau) p_m(\tau).$$
Therefore $\tilde{V}_\tau$ has the same eigenvalues and the eigenvectors $\bar{p}_m := G_\tau p_m$, which establishes the spectral representation

$$\tilde{V}_\tau \tilde{\psi}_n(\cdot, \tau, \cdot) = \sum_m \lambda_m(\tau) \tilde{\psi}_n(\cdot, 0, \cdot) \cdot \bar{p}_m(\tau),$$

where the scalar product is

$$\tilde{\psi}_n \cdot \bar{p}_m := \int_{\mathbb{T}^{dN-1}} \tilde{\psi}_n \cdot \bar{p}_m G_{\tau}^{-2} dX_0.$$

The representation (7.3) is used in the next section to establish bounds on $\partial_X \tilde{\psi}_n$.

7.2. Derivatives of the wave function. Differentiation of the Schrödinger equation (7.2) implies that the derivative $\zeta := \partial_X \tilde{\psi}_n$ satisfies

$$i \dot{\zeta} = \tilde{V}_\tau \zeta + \partial_X \tilde{V}_\tau \tilde{\psi}_n(\tau),$$

which has the integral representation

$$\zeta(\tau) = S_{\tau,0} \zeta_0 + \int_0^\tau S_{\tau,r} \partial_X \tilde{V}_\tau \tilde{\psi}_n(r) \, dr.$$  

Assume that

$$i \dot{\omega} = \tilde{V} \omega + q,$$

that is $\omega = S_{\tau,0} \omega_0 + \int_0^\tau S_{\tau,r} q(r) \, dr$. The spectral representation (7.3) and $\omega = \sum_m \omega_m \bar{p}_m$ imply that

$$i \sum_m \dot{\omega}_m \bar{p}_m = \sum_m \lambda_m \omega_m \bar{p}_m - i \sum_m \omega_m \dot{p}_m + q,$$

which yields

$$\omega_m(\tau) = e^{-i \int_0^\tau \lambda_m(r) \, dr} \omega_m(0) - \int_0^\tau e^{-i \int_s^\tau \lambda_m(r) \, dr} \left( \sum_j \omega_j(s) \hat{p}_j(s) \right) \cdot \bar{p}_m(s) \, ds$$

$$- i \int_0^\tau e^{-i \int_s^\tau \lambda_m(r) \, dr} q_s \cdot \bar{p}_m(s) \, ds.$$  

(7.6)

The initial assumption $\zeta_0 = \mathcal{O}(1)$ and $\hat{p}_j = \partial p_j / \partial X \circ dX / d\tau = \mathcal{O}(M^{-1/2})$, established from the bound $\partial_X p = \mathcal{O}(1)$ by (2.10) and $dX / dt = p = \mathcal{O}(1)$ by (2.5) using $V_n = \mathcal{O}(1)$, together with $\tau = \mathcal{O}(M^{1/2})$ shows that the two first terms in the right hand side of (7.6) (and the first in (7.4)) leads to the bound

$$S_{\tau,0} \zeta_0 = \mathcal{O}(1).$$

To establish a similar bound on the integral in the last term in (7.6) (and the second term in (7.4)) is subtle since $q = \partial_X \tilde{V}_\tau \tilde{\psi}_n(r) = \mathcal{O}(1)$ while $\tau = \mathcal{O}(M^{1/2})$, so that oscillatory cancellation has to be used. We will use an assumption on a continuum limit of a spectral
decomposition. Let the eigenvalues \( \{ \lambda_m(r) \mid m \in \mathbb{N} \} \) be in increasing order, satisfying \( \tilde{V}_r \tilde{p}_m(r) = \lambda_m(r) \tilde{p}_m(r) \) and define the average

\[
\bar{\lambda}_m(s) := (\tau - s)^{-1} \int_s^\tau \lambda_m(r) dr.
\]

We have the representation

\[
\sum_m e^{-i(\tau-s)\bar{\lambda}_m} q_s \cdot \tilde{p}_m(s) \tilde{p}_m(\tau) = \sum_{\lambda_k} \sum_{m: \lambda_m=\lambda_k} \partial_X \tilde{V}_\tau \tilde{\psi}_n(s) \cdot \tilde{p}_m(s) \tilde{p}_m(\tau).
\]

Remark 6.2 motivates that a change in the eigenvalue of order \( \delta \) perturbs each eigenstate \( \tilde{p}_m \) with an amount \( O(\delta N^{-1}) \), so that the sum over all eigenstates can have a change proportional to \( \delta = \bar{\lambda}_{k+1} - \bar{\lambda}_k \) as assumed in (7.7).

The large mass \( M \) implies that the eigenvalues \( \{ \lambda_m \} \) almost form a continuum with

\[
\Delta \bar{\lambda}_m = \bar{\lambda}_{m+1} - \bar{\lambda}_m = O(M^{-1}),
\]

as seen by adding another non interacting particle, which yields \( (\tau - s) \Delta \bar{\lambda}_m = o(1) \). The representation implies \( \sum \lambda_m f_M(\bar{\lambda}_m; \tau) \Delta \bar{\lambda}_m = \partial_X \tilde{V}_\tau \tilde{\psi}_n(\tau) \). Assume that \( f_M \to f \) in \( L^1(\mathbb{R}) \), then we have the Fourier integral limit

\[
\lim_{M \to \infty} \sum_{\lambda_m} e^{-i(\tau-s)\lambda_m} f_M(\bar{\lambda}_m) \Delta \bar{\lambda}_m = \int_{\mathbb{R}} e^{-i(\tau-s)\lambda} f(\lambda) d\lambda =: \hat{f}(\tau - s)
\]

and assume that \( f \) and its second derivative are bounded in \( L^1(\mathbb{R}) \), as a function of \( \lambda \), i.e. there is a constant \( C \) such that

\[
\int_{\mathbb{R}} |\partial_\lambda^2 f(\lambda)| + |f(\lambda)| \ d\lambda \leq C
\]

then

\[
\| \hat{f} \|_{L^\infty(\mathbb{R})} + \| \tau^2 \hat{f} \|_{L^\infty(\mathbb{R})} \leq C
\]

which implies

\[
|\hat{f}(\tau)| \leq \frac{C}{1 + \tau^2}
\]

so that \( \hat{f}(\tau - s) \) belongs to \( L^1(\mathbb{R}) \), as a function of \( s \). We conclude by integration over \( s \) in (7.6) that

\[
\zeta_\tau = O(1).
\]

Equation (2.10) for \( \partial_X p \) shows that \( \partial_X G \) also is bounded, provided \( |\partial_X XV_n| + |\partial_X V_n| = O(1) \) and the initial data \( \partial_X p|_I \) is bounded. Consequently \( \partial_X \psi_n \cdot \partial_X \psi_n = O(1) \) as \( M \to \infty \). The
second derivative $\Delta x_0 \tilde{\psi}_n$ can be estimated similarly by using instead $q = 2\partial_{x_0} \tilde{V} \partial_{x_0} \tilde{\psi}_n + \Delta x_0 \tilde{V} \tilde{\psi}_n$.

Reduced $L^1$-regularity $f \in W^{\beta,1}(\mathbb{R})$, with $\beta \in (0,1)$ derivatives in $L^1$ instead of two derivatives in $L^1$, implies

$$|\hat{f}(\tau)| \leq \frac{C}{1 + |\tau|^\beta}$$

and $\int_0^{M^{1/2}} |\hat{f}(\tau)| d\tau = O(M^{(1-\beta)/2})$; also this bound shows that the WKB-Ansatz $\psi_n e^{iM^{1/2}q_n}$ makes sense, since then $|\partial_{X_j} \psi| = O(M^{1-\beta/2}) \ll M^{1/2}$. If $\beta > 1$ we have $|\partial_{X_j} \psi| = O(1)$.

7.3. **Discrete spectrum.** This section verifies that the bilinear form

$$\int_{\mathbb{T}^{3(J+N)-1}} v \tilde{V}_v \, v + \gamma v^2 \, dx dX_0$$

is continuous and coercive on $H^1(\mathbb{T}^{3(J+N)-1})$, which implies that the spectrum of $\tilde{V}$ is discrete by the theory of compact operators, see [16]. Let $r := |x^j - X^n|$. Integrate by parts, for any $\epsilon > 0$, to obtain

$$-\int_0^R \frac{1}{|x^j - X^n|} v^2 r^2 dr = -\int_0^R \frac{1}{r} v^2 r^2 dr$$

$$= -\int_0^R v^2 \partial_r r^2 dr$$

$$= \int_0^R v \partial_r v \, r^2 dr + \left[ \frac{v^2 r^2}{2} \right]_{r=0}^{r=R}$$

$$\geq -\left( \int_0^R v^2 r^2 dr \int_0^R (\partial_r v)^2 r^2 dr \right)^{1/2} + \left[ \frac{v^2 r^2}{2} \right]_{r=0}^{r=R}$$

$$\geq -\frac{1}{2\epsilon} \int_0^R v^2 r^2 dr - \frac{\epsilon}{2} \int_0^R (\partial_r v)^2 r^2 dr + \left[ \frac{v^2 r^2}{2} \right]_{r=0}^{r=R}$$

and integrate the representation $v^2(R) R = v^2(\rho) R + \int_\rho^R 2v \partial_\rho v R \, d\rho$ to estimate the last term

$$v^2(R) \frac{R^2}{2} = \int_{R/2}^R v^2(\rho) R \, d\rho + \int_{R/2}^R 2v \partial_\rho v R \, d\rho$$

$$\geq \int_{R/2}^R v^2(\rho) R \, d\rho - \int_{R/2}^R \left( \int_\rho^R (\partial_\rho v)^2 r^2 R^{-1} \, dr \right)^{1/2} v^2 R^3 r^2 \, dr$$

$$\geq \int_{R/2}^R v^2(\rho) R \, d\rho - \frac{\epsilon}{4} \int_{R/2}^R (\partial_\rho v)^2 r^2 \, dr - \frac{1}{4\epsilon} \int_{R/2}^R v^2 R^4 r^2 \, dr$$

which shows that

$$-\int_0^R \frac{1}{|x^j - X^n|} v^2 r^2 dr \geq -\epsilon \int_0^R (\partial_r v)^2 r^2 dr - \frac{5}{\epsilon} \int_0^R v^2 R^4 r^2 \, dr.$$
Similar bounds for the other interaction terms in $V$ implies that the bilinear form is coercive
\[
\int_{T^{3}(J+N)-1}v\bar{V}_v + \gamma v^2 \, dx\, dX_0 \geq \int_{T^{3}(J+N)-1} \frac{1}{4} \sum_{j=1}^{J} |\partial_x^j v|^2 + \frac{1}{4M} \sum_{n=1}^{N} |\partial_X^n v|^2 + v^2 \, dx\, dX_0,
\]
for $\gamma \geq 60(MN + J)$. Analogous estimates show that the bilinear form is also continuous, i.e. there is a constant $C$ such that
\[
\int_{T^{3}(J+N)-1}v\bar{V}_v + \gamma vw \, dx\, dX_0 \leq C \|v\|_{H^1(T^{3}(J+N)-1)} \|w\|_{H^1(T^{3}(J+N)-1)}.
\]
The combination of coercivity and continuity in $H^1(T^{3}(J+N)-1)$ implies, by the theory of compact operators, that the spectrum of $\bar{V}$ consists of eigenvalues with orthogonal eigenvectors in $L^2(T^{3}(J+N)-1)$, see [16].

7.4. The Born-Oppenheimer approximation. To better understand the evolution (7.2) of $\tilde{\psi}_n$, we use the decomposition $\psi = \psi_0 + \psi^\perp$, where $\psi_0(\tau)$ is an eigenvector of $\bar{V}$ satisfying $V_\tau \psi_0(\tau) = \lambda_n(\tau) \psi_0(\tau)$ for an eigenvalue $\lambda_n(\tau) \in \mathbb{R}$. This Ansatz is motivated by the residual
\[
R\psi_0 := i\dot{\psi}_0 - \bar{V}\psi_0 = O(M^{-1/2})
\]
being small, since by (2.25)
\[
\dot{\psi}_0 = \partial_X \psi_0 \dot{X} = O(M^{-1/2})
\]
\[
\bar{V}\psi_0 = (V - V_n)\psi_0 + O(M^{-1}) = O(M^{-1/2}),
\]
provided
\[
\psi^\perp \cdot \psi^\perp = O(M^{-1/2}),
\]
which for $\psi_0 = O(1)$ yields
\[
V_n = \frac{(\psi_0 + \psi^\perp) \cdot V_\tau (\psi_0 + \psi^\perp)}{(\psi_0 + \psi^\perp) \cdot (\psi_0 + \psi^\perp)} = \lambda_n(\tau) + O(M^{-1/2}).
\]
We have $i\dot{\psi}^\perp = \bar{V}\psi^\perp - R\psi_0$ and by (7.2)
\[
\psi^\perp(\tau) = S_{\tau,0} \psi^\perp(0) - \int_{0}^{\tau} S_{\tau,s} R\psi_0(s) \, ds,
\]
so that (7.5) can be applied with $q = R\psi_0$ and we obtain as in (7.10)
\[
\psi^\perp(\tau) = O(M^{-1/2}),
\]
which also verifies that the bound (7.12) holds, if the initial data satisfies $\psi^\perp(0) = O(M^{-1/2})$ and the corresponding function
\[
f_M(\bar{\lambda}_k) \Delta \bar{\lambda}_k := \sum_{m : \bar{\lambda}_k = \bar{\lambda}_m} R\psi_0(s) \cdot p_m(s) \, p_m(\tau)
\]
satisfies (7.9).
Remark 7.1 (The Madelungen equation). An alternative to (2.6) is to instead include the coupling term $-\frac{1}{2M} \sum_j \Delta X_j \psi_n$ in the eikonal equation, which leads to the so called Madelungen equations [35]. Near the minima points, where $E - V_n(X) = 0$, the perturbation $-\psi_n \cdot \frac{1}{2M} \sum_j \Delta X_j \psi_n$ can be negative and then there is no real solution $\partial_X \theta_n$ to the corresponding eikonal equation. To have a non real velocity $\partial_X \theta_n$ is in our case not compatible with a classical limit and therefore we avoid the Madelungen formulation.

References

[1] Ariel G. and Vanden-Eijnden E., A strong limit theorem in Kac-Zwanzig model, Nonlinearity 22 (2009) 145.
[2] Barle G., Solutions de viscosité des équations de Hamilton-Jacobi, Springer-Verlag 1994.
[3] Bardi M. and Capuzzo-Dolcetta I., Optimal Control and Viscosity Solutions of Hamilton-Jacobi-Bellman Equations, Birkhäuser, 1997.
[4] Berezin F.A. and Shubin M.A., The Schrödinger Equation, Kluwer Academic Publishers, 1991.
[5] Briggs J. and Rost J.M., On the derivation of the time-dependent equation of Schrödinger, Foundations of Physics, 31 (2001), 693-712.
[6] Briggs J. Boonchui S. and Khemmani S., The derivation of the time-dependent Schrödinger equation, J. Phys. A: Math. Theor. 40 (2007) 1289-1302.
[7] Born M. and Oppenheimer R., Zur Quantentheorie die Molekeln, Ann. Physik 84 (1927) 457-484.
[8] Bornemann F.A., Nettesheim P. and Schütte C., Quantum-classical molecular dynamics as an approximation to full quantum dynamics, J. Chem. Phys. 105 (1996) 1074–1085.
[9] Cances E., Legoll F. and Stolz G., Theoretical and numerical comparison of some sampling methods for molecular dynamics, Math. Model. Num. Anal., 41 (2007) 351-389.
[10] Cances E., Defranceschi M., Kutzelnigg W., LeBris C. and Maday Y., Computational Chemistry: a primer, a Handbook of Numerical Analysis, X, North-Holland 2003.
[11] Cañizo J.A. and Díaz D.J., Spectral asymptotics in the semiclassical limit, London Mathematical Society, Lecture Note Series 268. Cambridge University Press (1999).
[12] Dür D., Goldstein S. and Lebowitz J.L., A mechanical model for the Brownian motion of a convex body, Z. Wahrscheinlichkeitstheori verw. Gebiete, 62 (1983) 427–448.
[13] Dür D., Goldstein S. and Lebowitz J.L., A mechanical model of Brownian motion, Commun. Math. Phys. 78 (1981) 507–530.
[14] Einstein A., Über die von der molekularischen Theorie der Wärme geforderte Bewegung von ruhenden Flüssigkeiten suspendierten Teilschen, Ann. Phys. 17 (1905) 549–560.
[15] Evans L.C., Partial Differential Equation, American Mathematical Society, Providence, RI, (1998)
[16] Feynman R.F., Statistical Mechanics: A Set of Lectures, Westview Press, 1998.
[17] Ford G. W. and Kac M., On the quantum Langevin equation, J. Statist. Phys. 46 (1987), 803–810.
[18] Ford G. W., Kac M. and Mazur P., Statistical mechanics of assemblies of coupled oscillators, J. Mathematical Phys. 6 (1965) 504–515.
[19] Fournais S., Hoffmann-Ostenhof M., Hoffmann-Ostenhof T. and Østergaard Sørensen T., Analytic structure of many-body Coulombic wave functions, arXiv:0806.1004v1, to appear in Comm. Math. Phys.
[20] Frenkel D. and Smith B., Understanding Molecular Simulation, Academic Press, 2002.
[21] Gardiner C.W., Quantum Noise, Springer-Verlag (1991).
[22] Gibbs J.W., Elementary Principles in Statistical Mechanics, New York, Charles Scribner’s sons, 1902.
[23] Hagedorn G.A., A time-dependent Born-Oppenheimer approximation, Commun. Math. Phys., 77 (1980) 1–19.
[25] Hald O. H. and Kupferman R., *Asymptotic and numerical analysis for mechanical models of heat baths*, J. Statist. Phys. **106** (2002) 1121–1184.

[26] Helffer B., *Semi-classical Analysis for the Schrödinger Operator and Applications*, Lecture Notes in Mathematics 1336 Springer Verlag 1988.

[27] Kadanoff L., *Statistical Physics: Statistics, Dynamics and Renormalization*, World Scientific, 2000.

[28] Kozlov V.V., *Thermodynamics of Hamiltonian systems and Gibbs distribution*, Doklady Mathematics, **61** (2000), 123-125. Translated from Doklady Akademii Nauk. **370** (2000) 325-327.

[29] Kupferman R. and Stuart A.M., *Fitting SDE models to nonlinear Kac-Zwanzig heat bath models*, Physica D **199** (2004) 279–316.

[30] Kupperman R., Stuart A.M., Terry J.R. and Tupper P.F., *Long-term behaviour of large mechanical systems with random initial data*, J. Stoch. Dyn. **2** (2002) 533–562.

[31] Langevin P., *On the theory of Brownian movement*, C.R. Acad. Sci. **146** 530 (1908), (translation Am. J. Phys. **65** 1079, 1997).

[32] Le Bris C., *Computational chemistry from the perspective of numerical analysis*. Acta Numer. **14** (2005), 363–444.

[33] Lia X., Tully J.C., Schlegel H.B. and Frisch M.J., *Ab initio Ehrenfest dynamics*, J. Chem. Phys. **123** (2005) 084106

[34] Lieb Elliot, *The stability of matter*, Rev. Mod. Phys. **48** (1976), 553-569.

[35] Madelung E., Z. Phys. **40** 322 (1926).

[36] Marx D. and Hutter J., *Ab initio molecular dynamics: Theory and implementation*, *Modern Methods and Algorithms of Quantum Chemistry*, J.Grotendorst(Ed.), John von Neumann Institute for Computing, Jülich, NIC Series, Vol. 1, ISBN 3-00-005618-1, pp. 301-449, 2000.

[37] Mott N.F., Proc. Camb. Phil. Soc. **27** (1931) 553.

[38] Panati G., Spohn H. and Teufel S., *The time-dependent Born-Oppenheimer approximation*, Math. Mod. Numer. Anal.

[39] Schrödinger E., *Collected papers on Wave Mechanics*, Blackie and Son, London (1928).

[40] Stuart A.M. and Warren J.O., *Analysis and experiments for a computational model of a heat bath*, J. Stat. Phys. **97** (1999) 687–723.

[41] Tanner D.J., *Introduction to Quantum Mechanics: A Time-dependent Perspective*, University Science Books, 2006.

[42] Tully J.C., *Mixed quantum-classical dynamics*, Faraday Discuss., **110** (1998) 407–419.

[43] Tully J.C., *Modern Methods for Multidimensional Dynamics Computation in Chemistry*, ed. D. L. Thompson, World Scientific Singapore, 1998, ch. 2.

[44] Zwanzig R., *Nonlinear generalized Langevin equations*, J. Stat. Phys. **9** (1973) 215–220.

Department of Mathematics, Kungl. Tekniska Högskolan, 100 44 Stockholm, Sweden

E-mail address: szepessy@kth.se