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Wouter Scharpach

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PROEFSCHRIFT

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door

Wouter Leopold Johannes Scharpach

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Het onderzoek dat in dit proefschrift wordt beschreven is uitgevoerd in overeenstemming met de TU/e Gedragscode Wetenschapsbeoefening.

# Abstract

In this thesis, we study the initial-value problem associated with a class of time-dependent Kohn–Sham equations coupled with Newtonian nuclear dynamics, which describes the nonadiabatic dynamics of molecular, spin-unpolarised systems. The time-dependent Kohn–Sham equations, which form a quantum-mechanical description of the electronic evolution, serve as an approximation of the time-dependent Schrödinger equation. The effective potential in the Kohn–Sham description includes an unknown part, the exchange-correlation potential. We study the Kohn–Sham equations in a generalised form of the so-called local density approximation: in this generalisation, the correlation term is set to zero, and the exchange term is a pure-power exchange term with various ranges of exponents as parameters. Using the mean-field Ehrenfest approach, which is a nonadiabatic mixed quantum-classical dynamics method, the time-dependent Kohn–Sham equations are coupled to a classical-mechanical description of the nuclear dynamics. The resulting system is a Hamiltonian system, in which the total energy and the electronic charge are conserved quantities over time. In this thesis, we show local-in-time existence and uniqueness of solutions to the initial-value problem in the Sobolev space $H^2$ for a certain range of exponents in the pure-power exchange term. We also show, under a conjecture on convergence, results towards global existence of weak solutions in the setting of the Sobolev space $H^1$ for another range of exponents in the pure-power exchange term, including the physically meaningful value that appears in the original local density approximation.

# List of publications

Below, a list is given of manuscripts (including those in press, submitted and in preparation) to which the author has contributed during his doctoral studies. The main results of these studies, which mostly stem from the latter two manuscripts in the list, are presented in this dissertation.

1. **Excited-state electronic structure of molecules using many-body Green's functions: Quasiparticles and electron–hole excitations with VOTCA-XTP**
   G. Tirimbò, V. Sundaram, O. Çaylak, W. Scharpach, J. Sijen, C. Junghans, J. Brown, F. Zapata Ruiz, N. Renaud, J. Wehner, B. Baumeier
   The Journal of Chemical Physics **152**, 114103 (2020)

2. **Time-Dependent Density Functional Theory and Green's Functions Methods with the Bethe–Salpeter Equation**
   W. Scharpach, Z. Chen, V. Sundaram, B. Baumeier
   in: *Excited States and Photodynamics: From Photobiology to Photomaterials.* Comprehensive Computational Chemistry, Elsevier (*in press*)

3. **Local existence and uniqueness of solutions to the time-dependent Kohn–Sham equations coupled with classical nuclear dynamics**
   B. Baumeier, O. Çaylak, C. Mercuri, M. Peletier, G. Prokert, W. Scharpach
   (*submitted*)

4. **Towards global existence of weak solutions to the time-dependent Kohn–Sham equations coupled with classical nuclear dynamics**
   B. Baumeier, C. Mercuri, M. Peletier, W. Scharpach
   (*in preparation*)

# Contents

# Chapter 1

# Introduction and background

In this thesis, we study the existence and uniqueness of solutions to initial-value problems associated with a class of time-dependent Kohn–Sham equations coupled with Newtonian nuclear dynamics, which describe the non-adiabatic dynamics of a molecular, spin-unpolarised system.

In the following equations,

$$\psi_k = \psi_k(x,t), \qquad X_K = X_K(t) \in \mathbb{R}^3, \qquad x \in \mathbb{R}^3, t \geq 0,$$

and we set

$$\rho := \sum_{k=1}^{N_{\mathrm{el}}} |\psi_k|^2,$$

with the convolution

$$\big(|\cdot|^{-1} * \rho\big)(x) = \int \frac{\rho(x')}{|x-x'|} \mathrm{d}x'.$$

The equations are given by

$$i\dot{\psi}_k = -\tfrac{1}{2}\Delta_x \psi_k - \sum_{K=1}^{N_{\mathrm{nuc}}} \frac{Z_K}{|\cdot - X_K|}\psi_k + \bigg(\frac{1}{|\cdot|} * \rho\bigg)\psi_k + \lambda\rho^{q-1}\psi_k, \quad (1.1a)$$

$$\ddot{X}_K = \frac{Z_K}{M_K}\bigg[\int \frac{x - X_K}{|x-X_K|^3}\rho(x)\mathrm{d}x + \sum_{L=1, L\neq K}^{N_{\mathrm{nuc}}} Z_L \frac{X_K - X_L}{|X_K - X_L|^3}\bigg], \quad (1.1b)$$

with $k \in \{1, \ldots, N_{\mathrm{el}}\}$, $K \in \{1, \ldots, N_{\mathrm{nuc}}\}$ for given $N_{\mathrm{nuc}}, N_{\mathrm{el}} \in \mathbb{N}$. Also, $Z_K \in \mathbb{N}$ and $M_K \geq 0$ are given. Further, we consider parameters $\lambda \in \mathbb{R}$ and $q > 1$.

The time-dependent Kohn-Sham equations (1.1a) then describe the electronic evolution in terms of single-particle wave functions $\psi_k$, and have been extensively considered as an approximation to the time-dependent Schrödinger equation, which reduces the electronic dynamics to a single-particle description based on the density function $\rho$. Here, the last term at the right-hand side is an approximation to a more general term, called the 'exchange-correlation term', which in the fundamental theory is not explicitly known. As will be shown in Chapter 3, which describes the above sets of equations, this is the main difficulty in the time-dependent Kohn–Sham approach: there does not exist a closed-form expression for this term, by which one has to resort to approximations and numerical presentations. Our specific choice in (1.1) is an approximation of the exchange part of the 'local-density approximation'; this way, we are able to study this term theoretically. In our approximation, we have parametrised this exchange part using the parameters $\lambda \in \mathbb{R}, q > 1$ to a generalisation in the form of a pure-power exchange term, for which the physically meaningful value in the exponent equals $q = 4/3$. The correlation part of the exchange-correlation term is put to zero. We will study the local-density approximation and our approximation of the exchange-correlation in more detail in Section 3.1.
The time-dependent Kohn-Sham equations (1.1a) are coupled with the equations (1.1b), which describe the nuclear dynamics.

## 1.1 Summary of the main results in the thesis

In this thesis, we study the Kohn–Sham functions $\psi_k$ as elements of the Sobolev spaces $H^2(\mathbb{R}^3)$ and $H^1(\mathbb{R}^3)$ (see also Appendix A.2) in order to arrive towards well-posedness results. This study yields the following results.

In the setting of $H^2$, we prove a local-in-time existence and uniqueness result in the range $[7/2, +\infty)$ for $q$.

**Theorem.** *Let $q \geq 7/2$ and $\lambda \in \mathbb{R}$. Further, let $\psi^0 \in H^2\big(\mathbb{R}^3; \mathbb{C}^{N_{\mathrm{el}}}\big)$, $V^0 \in \mathbb{R}^{3N_{\mathrm{nuc}}}$ and $X^0 \in \mathbb{R}^{3N_{\mathrm{nuc}}}$ be given, with $X^0_K \neq X^0_L$ for $K \neq L$.*

*Then, there exists $\tau > 0$ such that the initial-value problem associated to the system (1.1) with $\psi(0) = \psi^0$, $X(0) = X^0$ and $\dot{X}(0) = V^0$ has a unique solution $(\psi, X)$ in the function space*

$$C^1\big([0,\tau]; L^2(\mathbb{R}^3; \mathbb{C}^{N_{\mathrm{el}}})\big) \cap C^0\big([0,\tau]; H^2(\mathbb{R}^3; \mathbb{C}^{N_{\mathrm{el}}})\big) \times C^2\big([0,\tau]; \mathbb{R}^{3N_{\mathrm{nuc}}}\big).$$

The proof of the above theorem combines Yajima's theory for time-dependent, linear Hamiltonians with Duhamel's principle based on suitable Lipschitz estimates on the non-linearity in the right-hand side of (1.1a).

In the setting of $H^1$, we investigate the range $1 < q \leq 5/3$, so including the physically meaningful value $q = 4/3$, and the case $\lambda < 0$, which also corresponds to its value in the original formulation of the local density approximation. We use a Galerkin-type approximation method, based on the variational formulation for the system (1.1). We first prove existence of solutions $(\psi^n, X^n)$ in the space $C^1\big([0,T];H^1\big) \times C^2\big([0,T];\mathbb{R}^{3N_{\mathrm{nuc}}}\big)$ for arbitrary $T > 0$ to the truncated system of order $n \in \mathbb{N}$

$$\begin{aligned}
&\big(i\dot{\psi}_k^n(t), \phi^\nu\big)_{L^2} = \tfrac{1}{2}(\nabla_x \psi_k^n(t), \nabla_x \phi^\nu)_{L^2} + \\
&\Big( -\sum_{K=1}^{N_{\mathrm{nuc}}} \frac{Z_K}{|x - X_K^n|}\psi_k^n(t) + \int \frac{\rho^n(t,x')}{|\cdot - x'|}\mathrm{d}x'\psi_k^n(t) - |\lambda|[\rho^n(t)]^{q-1}\psi_k^n(t), \phi^\nu \Big)_{L^2},
\end{aligned} \tag{1.2a}$$

$$\begin{aligned}
\ddot{X}_K^n(t)\cdot Y &= Z_K \int \rho(t,x)\frac{x - X_K^n(t)}{|x - X_K^n(t)|^3}\mathrm{d}x \cdot Y \\
&\quad + \sum_{L\neq K}^{N_{\mathrm{nuc}}} Z_K Z_L \frac{X_K^n(t) - X_L^n(t)}{|X_K^n(t) - X_L^n(t)|^3}\cdot Y,
\end{aligned} \tag{1.2b}$$

$$\psi^n(0) = \psi^{n0} = \sum_{\nu=1}^{n} a_{k,\nu}^0 \phi^\nu, \qquad X^n(0) = X^{n0}, \qquad \dot{X}^{n0} = V^0. \tag{1.2c}$$

Here, $Y \in \mathbb{R}^3$, and the approximated solutions $\psi^n$ of order $n \in \mathbb{N}$ are of the form

$$\psi_k^n(t) = \sum_{\nu=1}^{n} a_{k,\nu}^n(t)\phi^\nu \in \mathrm{span}\{\phi^\nu\}_{\nu=1}^n \subset W,$$

with $a_{k,\nu}^n$ time-dependent scalar coefficients of class $C^1$ in $\mathbb{C}$ and $\phi^\nu$ the (orthonormal) eigenvectors of the eigenvalue problem $-\Delta_x\phi + |x|^2\phi = E\phi$ on $x \in \mathbb{R}^3$, which form a basis of the Hilbert space

$$W := \Big\{\phi \in H^1(\mathbb{R}^3)\Big| \int |x|^2|\phi|^2\mathrm{d}x < \infty\Big\}.$$

Then, we perform a convergence argument in the limit $n \longrightarrow \infty$, using the following conjecture.

**Conjecture.** *Let $T > 0$ be arbitrary, and let $\{\psi^n, X^n\}_{n\in\mathbb{N}}$ denote a sequence of solutions of (5.19). Then, for all $K = 1, \dots, N_{\mathrm{nuc}}$*

$$\int_0^T \int \frac{1}{|x - X_K^n(t)|^2} \big[|\psi^n(t,x)|^2 - |\psi(t,x)|^2\big] \mathrm{d}x\mathrm{d}t \xrightarrow{n\longrightarrow\infty} 0.$$

Eventually, we arrive at the following existence result on weak solutions. Here, $L^2L^2$ denotes the space $L^2L^2 = L^2\big((0,T); L^2(\mathbb{R}^3; \mathbb{C}^{N_{\mathrm{el}}})\big)$; see also Appendix A.2.

**Theorem.** *Let $1 < q \leq 5/3$ and $\lambda < 0$. Further, let $\psi^0 \in W, X^0 \in \mathbb{R}^{3N_{\mathrm{nuc}}}, V^0 \in \mathbb{R}^{3N_{\mathrm{nuc}}}$ such that $X_K^0 \neq X_L^0$ for $1 \leq K \neq L \leq N_{\mathrm{nuc}}$. Let $T > 0$ be arbitrary. Then, there exists a pair*

$$(\psi, X) \in L^2\big([0,T]; W^{N_{\mathrm{el}}}\big) \cap L^\infty\big((0,T); H^1(\mathbb{R}^3; \mathbb{C}^{N_{\mathrm{el}}})\big) \times C^0\big([0,T]; \mathbb{R}^{3N_{\mathrm{nuc}}}\big)$$

*which solves (1.1) in the sense that for all*

$$\begin{aligned} v &\in L^2\big([0,T]; H^1(\mathbb{R}^3)\big) \cap H^1\big([0,T]; L^2(\mathbb{R}^3)\big), \\ Y &\in C_{\mathrm{c}}^2\big((0,T); \mathbb{R}^3\big), \end{aligned}$$

*$(\psi, X)$ is a solution of the initial-value problem*

$$\begin{aligned} -(i\psi_k, \dot{v})_{L^2L^2} &= \tfrac{1}{2}(\nabla_x\psi_k, \nabla_x v)_{L^2L^2} + \Big( -\sum_{K=1}^{N_{\mathrm{nuc}}} \frac{Z_K}{|x - X_K|}\psi_k \\ &\qquad + \int \frac{\rho(x')}{|\cdot - x'|}\mathrm{d}x'\psi_k - |\lambda|\rho^{q-1}\psi_k, v \Big)_{L^2L^2}, \\ \int_0^T X_K(t)\cdot\ddot{Y}(t)\mathrm{d}t &= \int_0^T Z_K \int \rho(t,x)\frac{x - X_K(t)}{|x - X_K(t)|^3}\mathrm{d}x \cdot Y(t)\mathrm{d}t \\ &\qquad + \int_0^T \sum_{L\neq K}^{N_{\mathrm{nuc}}} Z_K Z_L \frac{X_K(t) - X_L(t)}{|X_K(t) - X_L(t)|^3}\cdot Y(t)\mathrm{d}t, \\ \psi(0) &= \psi^0, X(0) = X^0, \dot{X}(0) = V^0 \end{aligned}$$

The proof of the above theorem combines estimates on terms in the total energy with (mainly compactness) properties of $W$ and the approximated solutions to the truncated system (1.2).

The above results aim to provide a solid foundation for computational models typically employed in molecular modelling, which investigate the

same properties of molecular dynamics, viz. dynamics (e.g. in chemical reaction), and provide approximate numerical solutions in solving the same equations. These solutions obtained by the models may display behaviour one cannot directly expect or explain. This is especially important because of the wide class of different types of the aforementioned exchange-correlation term, of which the accuracy and stability highly depends on the types of the usage and objective of the models: see e.g. [LM22]. Unexpected or hard-to-explain behaviour can have different causes: it can happen due to *ill-posedness* of the underlying system of equations, needing theoretical research; *inaccuracy* or *instability* of the numerical methods the model uses, needing research to the numerical models themselves; or the behaviour is *accurate* after all, and one needs more understanding of the physics. Especially, existence and uniqueness results prove to be valuable in these situations, as if there *is no solution* to a system of equations, one can naturally expect weird behaviour of a numerical 'solution'; and if there *is no unique solution* to the problem, but the model expects it to be, the obtained numerical solution might in fact be a combination of several ones, without one knowing so. Computational models can either way benefit highly from theoretical research to the underlying problem, as it can explain the behaviour of the numerical solutions, and thus the models, and investigate their stability.

## 1.2 A brief introduction to quantum mechanics

In this section, we will briefly introduce the most fundamental elements of quantum mechanics, viz. the wave function and its probabilistic interpretation, and the Schrödinger equation, which describes its dynamics. Doing so based on the example of the quantum-mechanical atom model also lays the foundation for the later discussion of the many-electron problem and its implications for studies of dynamical electron-transfer processes, leading to the objective of the mathematical work in this thesis.

### 1.2.1 The atom model and energy quantisation

*Atoms* are the smallest units of ordinary matter forming solids, liquids, gases and plasmas. They, in turn, consist of the *nucleus* containing *protons* and *neutrons*, and the shell with *electrons*. Protons and electrons carry an elementary charge $e \approx 1.60 \cdot 10^{-19}\,\mathrm{C}$ with opposite signs, and

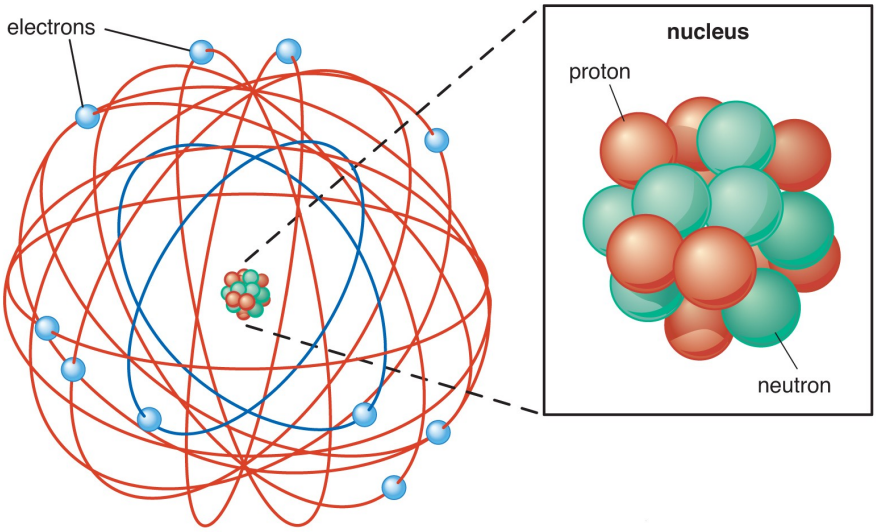


Figure 1.1: Depiction of a classical, planetary-type model of an atom, as often encountered in textbooks and encyclopædiæ. They misleadingly depict electrons as particles that follow "classical trajectories", while this is exactly *not* the case: this model cannot hold stable. *Image source:* Encyclopædia Britannica. [Edi22]

therefore are attracted to each other via the electromagnetic force. If the number of protons and electrons is equal, the atom is neutral, otherwise it is referred to as an ion. The same holds for all matter composed of atoms.

This basis structure of an atom was first deduced from the Rutherford experiment. It became apparent that the positive charge (hence the nucleus) is concentrated in a dense ($\sim 10^{-13} - 10^{-12}$ cm) region of space, while the electrons are occupying the remaining space of the atom, on the order of $10^{-8}$ cm. First models to describe this internal structure of an atom built on classical physics with an analogue of the planetary model of the solar system, as shown in Figure 1.1. With the electromagnetic force in place of gravity, the electrons supposedly orbit the nucleus on similarly well-defined trajectories as the planets orbit the sun, although some fundamental differences arise in the fact that the gravitational forces among celestial bodies are exclusively attractive, which is not the case for the electromagnetic force.

This classical, planetary-type-model model is problematic, however.

Even in the simplest case of the hydrogen atom, the single electron's trajectory is unstable. The angular acceleration acting on the charged particle in the electromagnetic field of the nucleus causes the emission of electromagnetic waves, which continuously carry energy away from the electron and, eventually, would make it spiral into the nucleus at a timescale of $\sim 10^{-11}$s. Our existence is evidence enough that there is something amiss in a classical picture of nature at very small, atomic scales.

Quantum mechanics offers a different perspective on this problem. Max Planck early on posed that electromagnetic radiation is emitted and absorbed in discrete amounts, which he coined *quanta*. Albert Einstein went further on this idea, and made the suggestion that the electromagnetic radiation itself consisted of particles, which were named *photons*. With this, Niels Bohr later revised the model of an atom postulating electrons moving on fixed *orbits* or *shells*, each of different, but fixed (quantised), energy levels. The quantisation of the energies implies that energy can only be lost in discrete amounts, "avoiding" the continuous energy loss of the planetary model.

### 1.2.2 Wave-particle duality

Besides the quantisation of the energy (which extends in general also to other quantities like energy, momentum, or angular momentum), the microscopic world also differs in other ways from our classical, everyday intuition, which include the wave-particle duality, the uncertainty principle as well as processes like tunnelling and entanglement. We will briefly talk about the wave-particle duality in the following, as it paves the way to a formalisation of quantum mechanics in a mathematical sense.

One of the best demonstration of the wave-particle duality, i.e., the fact that particle at small scales behave both like particles and like wave, is in the context of the *double-slit experiment*. When a bundle of coherent light impinges on a plate with two narrow slits and on a detection screen behind, a pattern is observed that is explained as a result of interference of elementary waves emanating from each slit. When one of the slits is blocked, individual intensity distributions, say $p_1$ and $p_2$ are recorded. When both slits are open, the observed intensity distribution $p$ is, however, *not* the sum of the two separate distributions: $p \neq p_1 + p_2$. This is unsurprising for light, as it was traditionally assumed to be an electromagnetic wave. However, when one repeats the same type of experiment with an electron beam instead of light, one observes the same

interference patterns. The electrons (plural!) behave like a wave. This has two important implications:

1. *Matter behaves in a random way.* We cannot predict where a particular electron will hit the screen; we can only determine the distribution or density of the locations. The behaviour of individual electrons is indeed intrinsically random;

2. *Matter shows wave-like properties.* The intensity pattern, or interference pattern, in the case when both slits are opened is wave-like: it is similar to when a wave would propagate through those slits. If, instead of the probability distributions $p_j$ for the cases when only slit $j$ is open, we would look at the corresponding wave intensities $|u_j|^2$, with $u_j = a_j e^{i\varphi_j}$, amplitudes $a_j$ and phases $\varphi_j$, we can observe that for the intensity $|u|^2$ for the case when both slits are opened, it holds that $|u|^2 \propto |u_1 + u_2|^2 \neq |u_1|^2 + |u_2|^2$. The mentioned randomness in the behaviour of electrons thus behaves according to laws from wave mechanics.

Both of these statements imply that a formal theory of quantum mechanics most be seen in a probabilistic setting. By *Born's rule*, named after Max Born, we know we can find a mathematical description of a probability by taking the square of the absolute value of a complex number. This is then known as a *probability amplitude*. By this, a quantum particle, like an electron, can be described by a *wave function*: this associated to each point in space a probability amplitude. Then, by the Born rule, we then get a *probability density function* for the position: this then describes whether the electron will be found at this position when an experiment would be performed in order to measure it. Note that this is the best we can obtain: there is no certainty where an electron can be found. Then, the *Schrödinger equation* can relate the set of probability amplitudes for one moment in time $t$ to the set of probability amplitudes for another moment in time $t'$. This will be outlined upon in the remainder of this section.

### 1.2.3 The wave function

The mathematical formulations in quantum mechanics enable a rigorous description of the theory. The main ingredient for this description comes from functional analysis, particularly *Hilbert spaces*: scalar inner product spaces which are also complete metric spaces with respect to the distance

function induced by their inner product. An example of a Hilbert space is the Lebesgue space $L^2(\mathbb{R}^3)$ (see also Section A.2), which is the space of square-integrable functions:

$$L^2(\mathbb{R}^3) := \Big\{ f : \mathbb{R}^3 \longrightarrow \mathbb{C} \text{ measurable} \;\Big|\; \int_{\mathbb{R}^3} |f(x)|^2 \mathrm{d}x < \infty \Big\}. \tag{1.4}$$

This space is an inner product space, with the inner product given by

$$(f, g)_{L^2(\mathbb{R}^3)} = \int_{\mathbb{R}^3} f(x) \cdot \overline{g(x)} \mathrm{d}x. \tag{1.5}$$

This inner product then induces the $L^2(\mathbb{R}^3)$ norm as follows:

$$\|f\|^2_{L^2(\mathbb{R}^3)} = \int_{\mathbb{R}^3} |f(x)|^2 \mathrm{d}x. \tag{1.6}$$

Since $L^2(\mathbb{R}^3)$ is complete with respect to the induced distance function $d(f, g) = \|f - g\|_{L^2(\mathbb{R}^3)}$ (under the equivalence relation $f \sim g$ if $f = g$ almost everywhere), it indeed forms a Hilbert space.

A main difference in the mathematical description of quantum physics from classical physics, is that measurable, physical quantities, called *observables*, like energy and momentum, are no longer viewed as function values in some phase space, but as *eigenvalues*; in particular, spectral values of linear operators on Hilbert spaces, mostly the $L^2$ space.

Any system in quantum mechanics is described by a state, which we call a *quantum state*. A quantum state is a mathematical entity, providing a *probability distribution* for outcomes of possible measurements. Any *mixture* of quantum states (so a countable convex combination) is again a quantum state. Any quantum states that cannot be written as such a mixture of other states are called *pure quantum states*; all other states are called *mixed quantum states*.

Pure states are also known as *state vectors*, or *wave functions*, a complex-valued function, depending on position (and/or momentum) and time. Then, it provides information in the form of probability amplitudes, about what measurements of a particle's energy, momentum, and other physical properties may yield. It resides in an either infinite- or finite-dimensional Hilbert space; usually this will be the $L^2$ space.

Let us for now consider, as an example, a single quantum particle, like an electron. Its wave function associates to each point in space a probability amplitude. When we apply the Born rule to all these amplitudes, we get a probability density function for the position where the

electron will be found. The collection of probability amplitudes associated to a certain moment of time are then related to the set for another moment of time by the *Schrödinger equation*. We will write this wave function for the single electron in $\mathbb{R}^3$, whose position can be denoted by $x \in \mathbb{R}^3$, then as a function of time $t \in \mathbb{R}$ as follows:

$$\Psi(x,t).$$

This function should then have the following properties, when considering the observations based on the double-slit experiment:

1. The probability distribution for the position of the particle is given by $x \longmapsto |\Psi(x,t)|^2$. This means that the probability that the particle is located in a subdomain $\Omega \subset \mathbb{R}^3$ at a certain time $t$ is

$$\int_\Omega |\Psi(x,t)|^2 \mathrm{d}x = \|\Psi(\cdot,t)\|^2_{L^2(\Omega)}.$$

   By this definition, we require the normalisation

$$\int_{\mathbb{R}^3} |\Psi(x,t)|^2 \mathrm{d}x = \|\Psi(\cdot,t)\|^2_{L^2(\mathbb{R}^3)} = 1.$$

2. The wave function $\Psi$ should satisfy a wave-like equation, given the wave-like properties of the particle. (This will be the *Schrödinger equation; see Section 1.2.4.*)

Looking back at the double-slit experiment, we can conclude that, with $\Psi_k$ denoting the state of a particle after it has passed through the shield with slit $k$ open, the wave function $\psi = \psi_1 + \psi_2$ describes the state with both slits opened. The interference pattern then indeed shows that $|\Psi|^2 \neq |\Psi_1|^2 + |\Psi_2|^2$.

With this definition of state vectors, we also have to define their *state space*, which is the space that should contain all possible states of the particle at a certain time $t$. In this thesis, we will consider (subsets of) $L^2$ spaces. Note that the normalisation condition just stated can be imposed when needed.

Of course, most cases we encounter involve more than one particle. Then, there is still only one wave function describing the quantum state of the full, many-body quantum system. We will consider systems including $N_{\mathrm{nuc}}$ nuclei and $N_{\mathrm{el}}$ electrons. In those cases, the wave function is written as

$$\Psi(x_1, \ldots, x_{N_{\mathrm{el}}}, X_1, \ldots, X_{N_{\mathrm{nuc}}}, t),$$

with $x_k \in \mathbb{R}^3$ the position of the $k^{\text{th}}$ electron, and $X_K \in \mathbb{R}^3$ the position of the $K^{\text{th}}$ nucleus. This altogether makes $\Psi$ a complex-valued function of $3(N_{\text{nuc}} + N_{\text{el}}) + 1$ variables.

### 1.2.4 The time-dependent Schrödinger equation

The wave function should satisfy some wave-like equation which describes its evolution. For simplicity, we consider here the for the case of a single electron, so $N_{\text{nuc}} = 0, N_{\text{el}} = 1$. We will write $\Psi(t)$ for the evolving states at time $t$, suppressing the position variables.

There are some principles this equation should satisfy:

1. *The causality principle*: The state $\Psi(t_0)$ should determine the states $\Psi(t)$ for all later times $t > t_0$;

2. *The superposition principle*: If $\Psi(t)$ and $\Psi'(t)$ are evolutions of states at a time $t$, any linear combination $\alpha\Psi(t) + \beta\Psi'(t)$ with $\alpha, \beta \in \mathbb{C}$ should also describe the evolution of some state at time $t$;

3. *The correspondence principle*: For "everyday situation", the quantum-mechanical description should resemble, or at least approximate the classical-mechanical description with which we are familiar.

What does that mean for the equation? The causality principle tells us $\Psi$ should satisfy a first-order time evolution equation:

$$\partial_t \Psi = A\Psi \tag{1.7}$$

for some operator $A$ which acts on the state space. The superposition principle then tells us $A$ should be a *linear* operator. The correspondence principle then gives us the way to determine the expression for $A$. Here, we employ the analogy, given by the correspondence principle, of wave optics in the quantum-mechanical description of nature with geometrical optics in the classical-mechanical description.

The *eikonal equation*

$$\partial_t \varphi = \pm c|\nabla_x \varphi| \tag{1.8}$$

gives the characteristics for how everyday light propagates along straight lines according to the laws of geometrical optics. Here, we call the real-valued function $\varphi(x, t)$ the *eikonal*, standing for the image of the wave

propagation, and $c$ stands for the speed of light. Just like electromagnetic radiation in general does, we also know that light has to obey Maxwell's equations, or more specifically for the electric field in a complex representation, in reduced form, the *wave equation*

$$\partial_t^2 u = c^2 \Delta_x u. \tag{1.9}$$

Here, we write the field as the complex-valued $u = e^{\frac{i\varphi}{\lambda}}$, with the real-valued function $a(x,t)$ as the amplitude, the eikonal $\varphi(x,t)$ as the phase, and $\lambda > 0$ as the wavelength. Here, we assume that $a$ and $\varphi$ and their derivatives behave nicely, meaning they are of order $\mathcal{O}(1)$ in terms of the wavelength. The eikonal equation then appears when we pass the high-frequency limit for microscopic wavelengths, that is, very small wavelengths compared to the typical object size, or $\lambda \downarrow 0$.

When differentiating, we obtain

$$\begin{aligned}
\partial_t u &= (\partial_t a + ia\partial_t\varphi/\lambda)e^{\frac{i\varphi}{\lambda}},\\
\partial_{x_j} u &= (\partial_{x_j} a + ia\partial_{x_j}\varphi/\lambda)e^{\frac{i\varphi}{\lambda}},\\
\lambda^2\partial_t^2 u &= \left[\lambda^2\partial_t^2 a + 2i\lambda\partial_t a\partial_t\varphi + i\lambda a\partial_t^2\varphi - a(\partial_t\varphi)^2\right]e^{\frac{i\varphi}{\lambda}},\\
\lambda^2\Delta_x u &= \left[\lambda^2\Delta_x a + 2i\lambda\nabla_x a\cdot\nabla_x\varphi + i\lambda a\Delta_x\varphi - a|\nabla_x\varphi|^2\right]e^{\frac{i\varphi}{\lambda}},
\end{aligned}$$

by which it follows from the wave equation (1.9) that

$$a(\partial_t\varphi)^2 = ac^2|\nabla_x\varphi|^2 + \mathcal{O}(\lambda).$$

Now, the short-wave approximation $\lambda \downarrow 0$ gives the eikonal equation (1.8) indeed.

Now, we want to obtain an equation in classical mechanics equivalent to the eikonal equation. This is the *Hamilton–Jacobi equation*

$$\partial_t S = -\frac{1}{2m}|\nabla_x S|^2 - V. \tag{1.10}$$

Here, the right-hand side contains a classical Hamiltonian function for a particle of mass $m$ moving along a potential $V(x)$, also which contains the gradient of a *classical action* $S(x,t)$. Now, we want to obtain an evolution equation that approximates the Hamilton–Jacobi equation similarly when moving to a classical-mechanical setting as the wave equation approximates the eikonal equation. The limit we pass here, instead of the high-frequency limit $\lambda \downarrow 0$, is the *classical limit* $\hbar \downarrow 0$, with the parameter $\hbar$ the *reduced Planck constant*, which is an atomic unit of action:

this means it has the dimensions of action, and is very small compared to a typical classical action for the system we consider. Let us make a similar ansatz for a solution to (1.7) as we did for the solution to the wave equation (1.9): that is, we assume $\Psi = ae^{iS/\hbar}$, with $\hbar$ indeed taking the function of the wavelength $\lambda$ before, and as the phase the classical action $S$ (satisfying the Hamilton–Jacobi equation (1.10)) instead of the eikonal $\varphi$. Also, we assume that the amplitude $a$ is independent of $\hbar$. Then, we obtain

$$\begin{aligned}
\partial_t \Psi &= (\partial_t a + ia\partial_t S/\hbar)e^{\frac{iS}{\hbar}}, \\
\partial_{x_j} \Psi &= (\partial_{x_j} a + ia\partial_{x_j} S/\hbar)e^{\frac{iS}{\hbar}}, \\
-\frac{\hbar^2}{2m}\Delta_x \Psi &= -\frac{1}{m}\big(\hbar^2 \Delta_x a + 2i\hbar \nabla_x a \cdot \nabla_x S + i\hbar a \Delta_x S - a|\nabla_x S|^2\big)e^{\frac{iS}{\hbar}},
\end{aligned}$$

by which it follows, using the Hamilton–Jacobi equation (1.10), that

$$i\hbar\partial_t \Psi = \left[i\hbar\partial_t a + a\left(\frac{1}{2m}|\nabla_x S|^2 + V\right)\right]e^{\frac{iS}{\hbar}}.$$

Since

$$i\hbar\partial_t a + \frac{\hbar^2}{2m}\Delta_x a + \frac{i\hbar}{m}\nabla_x a \cdot \nabla_x S = \mathcal{O}(\hbar) \xrightarrow{\hbar \downarrow 0} 0,$$

we see that $\Psi$ satisfies the equation

$$i\hbar\partial_t \Psi = -\frac{\hbar^2}{2m}\Delta_x \Psi + V\Psi \tag{1.11}$$

to a leading order with respect to $\hbar$. This equation is a simple form of the *Schrödinger equation*, and it approximates the Hamilton–Jacobi equation in the classical limit indeed. We can write (1.11) in the form of (1.7) with $A = -iH/\hbar$, with the operator

$$H = -\frac{\hbar^2}{2m}\Delta_x + \mathcal{V}.$$

We call the linear operator $H$ a *Schrödinger operator*. Note that $\mathcal{V}$ here is the multiplication operator associated with the potential function $V$, given by $\mathcal{V} : \Psi \longmapsto V\Psi$.

Now, we will consider, instead of a single electron, a more general case with several electrons and nuclei, say $N_{\mathrm{el}}$ and $N_{\mathrm{nuc}}$, with nuclear

| | | |
|---|---|---|
| *wave optics:* | | *geometric optics:* |
| wave equation | $\xrightarrow{\textit{high-frequency limit}}$ | eikonal equation |
| *quantum mechanics:* | | *classical mechanics:* |
| Schrödinger equation | $\xrightarrow{\textit{classical limit}}$ | Hamilton–Jacobi equation |

Table 1.1: Outline of the approximation in the "classical limit" according to the correspondence principle of the Schrödinger equation starting from the Hamilton–Jacobi equation, in an analogy to how the wave equation approximates the eikonal equation.

masses $M_K$ and charges $Z_K$. Note that electrons carry another degree of freedom, called *spin*, which is one of two types of angular momentum, the other being the orbital angular momentum; since we restrict ourselves to the discussion of spin-unpolarised systems, we will ignore spin for the remainder of the thesis. Then, (1.11) generalises to

$$i\partial_t \Psi = H\Psi, \qquad \Psi = \Psi(\overline{x}, X, t), \tag{1.12}$$

with the Schrödinger operator

$$\begin{aligned} H = &-\tfrac{1}{2}\sum_{K=1}^{N_{\text{nuc}}} \frac{\Delta_{X_K}}{M_K} + \tfrac{1}{2}\sum_{\substack{K,L=1,\\ K\neq L}}^{N_{\text{nuc}}} \frac{Z_K Z_L}{|X_K - X_L|} - \tfrac{1}{2}\sum_{k=1}^{N_{\text{el}}} \Delta_{x_k} \\ &+ \tfrac{1}{2}\sum_{\substack{k,\ell=1,\\ k\neq \ell}}^{N_{\text{el}}} \frac{1}{|x_k - x_\ell|} - \sum_{K=1}^{N_{\text{nuc}}}\sum_{k=1}^{N_{\text{el}}} \frac{Z_K}{|x_k - X_K|}. \end{aligned} \tag{1.13}$$

This way, a single partial differential equation, viz. (1.12), fully describes the behaviour of electrons and nuclei on a quantum level, and the terms in the Hamiltonian (1.13) correspond to kinetic energies and the electrostatic interaction between charged particles. It is tempting to try to solve (1.12) to obtain the dynamics of complex systems. If successful, it would offer invaluable insights into many fundamental processes in nature and device applications, and this way pave the way for many nature-inspired materials designs. For instance, plants manage to direct a series of dynamical processes, called *photosynthesis*, involving electrons created from the initial absorption of light to the synthesis of adenosine diphosphate (ADP) and the release of oxygen. What is striking about this meticulously directed chain of processes, is that nature succeeds to

do this very efficiently, with the processes taking place within a photocomplex with a lot of disorder, under nearly all conditions, and across vast distances (for electrons). In many synthetic materials, e.g., for the use in solar cells with similar objectives as an initial part of photosynthesis (namely, the absorption of light and so the creation of electrons), this level of mimicking nature has not been achieved so far.

As desirable as having insight from solutions to (1.12) may be, they are practically impossible to obtain. In the following, we will focus on approximate theories for the many-electron problem, leading us to the system of equations at the focus of this thesis.

## 1.3 Outline of the remainder of the thesis

In the previous sections, a general introduction to quantum mechanics, especially to the concepts and notions we will use from that theory, had been given. This has been done such that the reader now can get acquainted with the more involved ideas and discussions we put forward afterwards, and to give some intuition to the notion of usefulness of the results that are presented later on in this thesis. Given the discussed material in the previous section 1.2, we are now good to go in formulating what we would like to achieve in this thesis.

What do we want with all of this knowledge from the previous chapters? In principle, we can calculate quantum properties like the dynamics now, using the Schrödinger equation for the wave functions. But can we really do this? And how efficiently can this be done? And what can we say about the solutions? We can formulate what we would like to know and achieve, our objectives, in a less vague way and with more detail in the form of the following questions:

1. We have seen how in a (many-body) quantum system, so involving both nuclei and electrons, the dynamics is always coupled: the system dynamics involves both the nuclei and the electrons, and the quantum state is described by one many-body wave function.

   How to model the electronic-nuclear dynamics, which is coupled? We have seen this can be done by directly solving the Schrödinger equation, but how to do this efficiently? Can we get to a description, well-balanced between efficiency and accuracy, inside the formalism we use for the full, many-body quantum system, via suitable approximations and models?

2. Can we say something useful on the well-posedness solutions to the equations describing the mentioned approximations within these formulated models? In other words, are there ways to ensure short-time existence and uniqueness of these coupled solutions for the nuclear and electronic configurations on a certain temporal domain, in a certain functional setting for the single-particle wave functions?

3. Are there ways to formulate results on global existence of these solutions in a certain functional setting as well?

Question 1 will be answered in Chapter 2. The other questions will be treated in Chapters 4 and 5.

In Chapter 2, it will become apparent that we cannot treat the dynamics of a full many-body quantum system from a fully quantum-mechanical perspective. Therefore, the theory behind and methods within the framework of time-dependent density functional theory will be explained. Using this framework, we are able to separate the electronic and nuclear part of the coupled dynamics, by which there are two subsystems in the PDE describing the full quantum system; we then map the $N_{\mathrm{el}}$-electron problem describing the electronic part of the quantum dynamics to $N_{\mathrm{el}}$ single-particle problems for all electrons separately; and then at the same time we are able to study the nuclear dynamics in a classical-mechanical way. This results in the system we will study in this thesis.

In Chapter 3, we state the eventual system of equations under consideration, together with some considerations and notes on it: we write it as a Hamiltonian system with a variational formulation, and prove conservation in time of the total energy and the charge.

We set a further step in arriving at the desired results by formulating a certain methodology for the system under consideration. This involves, *inter alia*, a rewriting of the system in variational form, studies from perspectives on the Hamiltonian structure of the system. In this part, we set up a formulation using which we are able to investigate conserved quantities of the system under consideration, for example. These results will be formulated and used in order to arrive at the desired results later on in Chapters 4 and 5. The mathematical analysis outlined here is important, since by this we are able to get to results that qualify the coupled solutions to the eventual system we formulated in Chapter 2. Via this way, we are one step closer to performing validation analyses for

numerical solutions that arrive from simulations carried out by computational efforts. Why is all that interesting? Validation of the solutions is quite important, since it tells us something about what we can be certain about, and what we cannot be certain about. If solutions display strange behaviour one would not expect, the validation procedures can help in this.

# Chapter 2

# Theoretical framework

Photophysical processes, like photon absorption and emission, as well as dynamical processes, such as charge and energy transfer, result from the interaction between light and matter. If one looks at it more fundamentally, one of the instrumental processes here is the promotion of a material system (a molecule, a cluster of molecules, or a crystal) from its ground state to an electronically excited state. This part deals with an electronic-structure-theory method which allows us to describe such excited states from first principles: Time-dependent density-functional theory (TDDFT).

A fundamental aspect of TDDFT is, that it does not treat the many-, $N_{\mathrm{el}}$-electron problem explicitly in terms of many-electron wave functions as solutions to the Schrödinger equation (1.12): instead, they provide an effective description built on top of a reference ground state, which on its own is based on density-functional theory (DFT), the time-independent version of TDDFT. In TDDFT, we will then arrive at a governing set of $N_{\mathrm{el}}$ equations, which represent the excitation as coupled transitions between (in the ground state) occupied and unoccupied single-particle states.

In this part, we will discuss the theoretical foundations of TDDFT, starting with a brief recapitulation of conventional (time-independent) DFT, in order to organise the high amount of theoretical aspects and to present a self-contained story. A way to obtain excited-state information in this framework happens through the formulation of explicitly time-dependent equations, called the *Kohn–Sham equations*. For a sample of the extensive body of literature on both physical and mathematical aspects

of density-functional theory, its time-dependent version and the Kohn-Sham equations, the reader is referred to [HK64; Lie83; AC09; PK03; CMY12; KS65; Ull12].

Since the nuclei are assumed to be frozen in a certain fixed arrangement in the framework of (DFT and) TDDFT, we need an additional approach to incorporate the nuclear dynamics after all. The nuclear dynamics are important to incorporate in studying dynamical processes, in particular describing phenomena like electron-transfer reactions. In the point-nuclei approximation, we consider the nuclear dynamics to be classical in nature, and we use a so-called *mixed quantum-classical dynamics approach*. We will consider the *mean-field* or *Ehrenfest approach*. Combining the above, we will arrive at a system we will study further.

In the remainder of this thesis, we generally use *Hartree atomic units* (except for the derivation of the mean-field Ehrenfest method in Section 2.3.2, in which we have to perform a classical limit like in Section 1.2.4), which are named after Douglas Hartree. This is a system of natural units of measurement that is convenient for atomic physics and computational-chemistry calculations. In this system, we make a choice of physical units, such that the following four fundamental physical constants become 1 (multiplied by a coherent unit of this system):

- The *reduced Planck constant* $\hbar$, the atomic unit of action;
- the *elementary charge* $e$, the atomic unit of charge;
- the *Bohr radius* $a_0$, the atomic unit of length;
- the *electron mass*: $m_\mathrm{e}$, the atomic unit of mass.

This way, all charges are in units of the elementary charge, all positions are in units of the Bohr radius, and all masses are in units of the electron mass.

Furthermore, in the remainder of this thesis, we consider a quantum system that contains a number of $N_\mathrm{nuc} \in \mathbb{N}$ nuclei and $N_\mathrm{el} \in \mathbb{N}$ electrons. Furthermore, we will use the shorthands $X = (X_1, \ldots, X_{N_\mathrm{nuc}}) \in \mathbb{R}^{3N_\mathrm{nuc}}$ and $\overline{x} = (x_1, \ldots, x_{N_\mathrm{el}}) \in \mathbb{R}^{3N_\mathrm{el}}$.

## 2.1 Density-functional theory

In this section, we briefly recapitulate the basics of density-functional theory as a method to obtain an effective, single-particle description of

the electronic ground state of an atomic, molecular or solid many-particle system of $N_{\mathrm{nuc}}$ atoms and $N_{\mathrm{el}}$ electrons.

With the coordinates $X_K$ of the individual nuclei with masses $M_K$ charges $Z_K$ and $x_k$ of the individual electrons combined into the variables $X = (X_1, \ldots, X_{N_{\mathrm{nuc}}})$ and $\overline{x} = (x_1, \ldots, x_{N_{\mathrm{el}}})$, respectively, the (non-relativistic) many-body Hamiltonian reads

$$H = \underbrace{-\tfrac{1}{2}\sum_{K=1}^{N_{\mathrm{nuc}}} \frac{\Delta_{X_K}}{M_K}}_{\mathcal{T}_{\mathrm{nuc}}} + \underbrace{\tfrac{1}{2}\sum_{\substack{K,L=1,\\ K\neq L}}^{N_{\mathrm{nuc}}} \frac{Z_K Z_L}{|X_K - X_L|}}_{\mathcal{V}_{\text{nuc-nuc}}} \underbrace{-\tfrac{1}{2}\sum_{k=1}^{N_{\mathrm{el}}} \Delta_{x_k}}_{\mathcal{T}_{\mathrm{el}}} + \underbrace{\tfrac{1}{2}\sum_{\substack{k,\ell=1,\\ k\neq \ell}}^{N_{\mathrm{el}}} \frac{1}{|x_k - x_\ell|}}_{\mathcal{V}_{\text{el-el}}} \underbrace{-\sum_{K=1}^{N_{\mathrm{nuc}}}\sum_{k=1}^{N_{\mathrm{el}}} \frac{Z_K}{|x_k - X_K|}}_{\mathcal{V}_{\text{nuc-el}}}. \tag{2.1}$$

Here, $\mathcal{T}$ and $\mathcal{V}$ are the respective operators for the kinetic and potential energies involving the nuclear (nuc) and electronic (el) subsystems. The time evolution of the many-body wave function $\Psi(\overline{x}, X, t)$ is obtained by solving the time-dependent Schrödinger equation with as Schrödinger operator the Hamiltonian $H$, [Sch26] which in this case boils down to

$$i\partial_t \Psi = H\Psi, \qquad \Psi = \Psi(\overline{x}, X, t). \tag{2.2}$$

This time evolution then can be used to calculate expectation values of observables described by an operator $A$ as

$$(A(t))_\Psi = \iint \Psi(\overline{x}, X, t)\overline{A(t)\Psi(\overline{x}, X, t)}\mathrm{d}\overline{x}\mathrm{d}X. \tag{2.3}$$

allows – formally – to extract information about structural, electronic and optical properties of the system, as well as the dynamic response to an external perturbation (described by an additional potential term in (2.1)) as measured, e.g., by spectroscopic techniques.

In practice, however, (2.2) is exactly solvable only for $N_{\mathrm{nuc}} = N_{\mathrm{el}} = 1$, which numbers describe a hydrogen atom. This means that we need to explore approximations to make the problem tractable. The standard method of solving a partial differential equation such as (2.2) is the method of separation of variables: in this method, one makes the following product function ansatz:

$$\Psi(\overline{x}, X, t) = \Phi(\overline{x}, X)\alpha(t).$$

If the Hamiltonian in (2.1) is not explicitly time-dependent, its expectation value, the *total molecular energy* which we denote by $(H)_\Psi = E_{\mathrm{mol}}$, is constant according to (2.3), and the time evolution of the wave function is given by $\alpha(t) = Ce^{-iE_{\mathrm{mol}}t}$. The spatial component $\Phi(\overline{x}, X)$ of the wave function and the total energy are obtained as solutions of the *stationary Schrödinger equation*

$$H\Phi = E_{\mathrm{mol}}\Phi, \qquad \Phi = \Phi(\overline{x}, X). \tag{2.4}$$

Note that in (2.4) both $\overline{x}$ and $X$ are explicit variables of this eigenvalue problem. Since the nuclei are much heavier than the electrons, one can further assume that the electrons adjust instantaneously to the nuclear motion, i.e., the electrons move adiabatically. To express this situation in formal terms, we consider a *fixed arrangement* of nuclei $X$. The Hamiltonian representing the electronic system that interacts with the fixed nuclear configuration reads

$$H_{\mathrm{el}}(X) = \underbrace{\mathcal{T}_{\mathrm{el}} + \mathcal{V}_{\text{nuc-el}}(X)}_{\text{1-electron operator}} + \underbrace{\mathcal{V}_{\text{el-el}}}_{\text{2-electron operator}}. \tag{2.5}$$

In this situation, $X$ is no longer a variable of the electronic system, but a fixed parameter for the electronic degrees of freedom. The corresponding stationary electronic Schrödinger equation is given by

$$H_{\mathrm{el}}(X)\Phi_k(\overline{x}; X) = E_k(X)\Phi_k(\overline{x}; X), \qquad k = 1, \ldots, N_{\mathrm{el}}, \tag{2.6}$$

where $\{\Phi_k(\overline{x}; X), k = 1, \ldots, N_{\mathrm{el}}\}$ is a set of adiabatic electronic wave functions. Those can be used as a basis to expand the molecular wave function $\Phi(\overline{x}, X)$ according to

$$\Phi(\overline{x}, X) = \sum_{k=1}^{N_{\mathrm{el}}} \Xi_k(X)\Phi_k(\overline{x}; X). \tag{2.7}$$

Entering this *Born–Oppenheimer separated* wave function into (2.4) yields – after some steps [MK11] – a coupled set of equations for the coefficients $\{\Xi_k(X), k = 1, \ldots, N_{\mathrm{el}}\}$:

$$E_{\mathrm{mol}}\Xi_k(X) = [E_k(X) + \mathcal{T}_{\mathrm{nuc}} + \mathcal{V}_{\text{nuc-nuc}}]\Xi_k(X) + \sum_{\ell=1}^{N_{\mathrm{el}}} A_{k\ell}\Xi_\ell(X), \tag{2.8}$$

where the integrals $A_{k\ell}$ are matrix elements of the transition between electronic states $k$ and $\ell$ induced by the dynamics of the nuclei. In the adiabatic approximation it is assumed that $A_{\ell k} \equiv 0$, i.e., there are no transitions between different electronic states, and the nuclear motion for each electronic state $k$ is determined by

$$E_{\text{mol}}\Xi_k(X) = [E_k(X) + \mathcal{T}_{\text{nuc}} + \mathcal{V}_{\text{nuc-nuc}}]\Xi_k(X). \tag{2.9}$$

This describes the motion of the nuclei in an effective potential

$$V_k(X) = E_k(X) + V_{\text{nuc-nuc}}(X), \tag{2.10}$$

with $V_{\text{nuc-nuc}}$ the potential function associated with the potential operator $\mathcal{V}_{\text{nuc-nuc}}$.

### 2.1.1 Hartree–Fock theory

The electronic Schrödinger equation (2.6) is in practice still not solvable for many-body systems, due to the presence of the electron-electron interaction $\mathcal{V}_{\text{el-el}}$. Without it, the electronic Hamiltonian would simply be the sum of non-interacting single-particle Hamiltonians, i.e.,

$$H_{\text{el}}^0 = \sum_{k=1}^{N_{\text{el}}} h_k(x_k). \tag{2.11}$$

As these single-particle operators commute, i.e.,

$$[h_k(x_k), h_\ell(x_\ell)] = 0, \qquad k, \ell = 1, \ldots, N_{\text{el}},$$

the corresponding $N_{\text{el}}$-electron wave function $\Phi_k^0$ is simply a product of single-particle functions

$$\Phi_k^0(\overline{x}) = \prod_{\ell=1}^{N_{\text{el}}} \phi_{k_\ell}^0(x_\ell),$$

where $k_\ell$ indicates some permutation on the set $\{1, \ldots, N_{\text{el}}\}$, and the total energy is given by

$$E_k^0 = \sum_{\ell=1}^{N_{\text{el}}} \varepsilon_{k_\ell}^0.$$

However, according to the Pauli principle, the electronic wave functions must be antisymmetric with respect to particle exchange, and therefore must change sign whenever the coordinates of two electrons are

interchanged. To meet this requirement, the electronic wave function is constructed from single-particle functions $\phi_k$ as a so-called *Slater determinant* [Sla28]:

$$\begin{aligned}\Phi(\overline{x}) &= \frac{1}{\sqrt{N_{\mathrm{el}}!}}\det\big((\phi_k(x_\ell))_{k,\ell=1,\dots,N_{\mathrm{el}}}\big)\\ &= \frac{1}{\sqrt{N_{\mathrm{el}}!}}\begin{vmatrix}\phi_1(x_1) & \cdots & \phi_1(x_{N_{\mathrm{el}}})\\ \phi_2(x_1) & \cdots & \phi_2(x_{N_{\mathrm{el}}})\\ \vdots & \ddots & \vdots\\ \phi_{N_{\mathrm{el}}}(x_1) & \cdots & \phi_{N_{\mathrm{el}}}(x_{N_{\mathrm{el}}}).\end{vmatrix}\end{aligned} \tag{2.12}$$

The idea of the Hartree–Fock theory is that, instead of starting from predetermined single-particle functions and enforcing antisymmetry, we *start* from the requirement of antisymmetry, and use the variational principle to derive a set of equations that determine suitable effective single particles for the interacting case. The total electronic energy (suppressing the parametric dependence on $X$) for any given wave function $\Phi$ reads

$$E[\Phi] = (H_{\mathrm{el}})_\Phi = \int \Phi(\overline{x})\overline{H_{\mathrm{el}}\Phi(\overline{x})}\mathrm{d}\overline{x}. \tag{2.13}$$

The variational theorem states that this energy functional is minimal for the true ground-state wave function: i.e.,

$$E[\Phi] \geq E_0,$$

where $E_0$ is the ground-state energy. Now, let $\Phi^{\mathrm{HF}}$ denote the many-body wave function in Hartree–Fock theory as a Slater-determinant ansatz. By a variational principle, the energy as a functional of the determinant approximates the true ground-state energy $E_0$:

$$E[\Phi^{\mathrm{HF}}] = \frac{(H_{\mathrm{el}})_{\Phi^{\mathrm{HF}}}}{\|\Phi^{\mathrm{HF}}\|^2_{L^2(\mathbb{R}^{3N_{\mathrm{el}}})}} \geq E_0.$$

We now minimise the energy functional above via the effective single-particle functions $\phi_k$, under the constraint that they are normalised; this is achieved by

$$\partial_{\overline{\phi_k}}\Big[E[\Phi^{\mathrm{HF}}] - \sum_{k=1}^{N_{\mathrm{el}}}\varepsilon_k^{\mathrm{HF}}\big(\|\phi_k\|^2_{L^2(\mathbb{R}^3)} - 1\big)\Big] = 0.$$

This then yields a set of equations which allow us to determine the functions $\phi_k = \phi_k^{\mathrm{HF}}, k = 1, \ldots, N_{\mathrm{el}}$, which we call the *Hartree–Fock wave functions*:

$$(-\tfrac{1}{2}\Delta_x + \mathcal{V}_{\mathrm{ext}} + \mathcal{V}_{\mathrm{H}} + \mathcal{V}_{\mathrm{x}})\phi_k^{\mathrm{HF}} = \varepsilon_k^{\mathrm{HF}}\phi_k^{\mathrm{HF}}. \tag{2.14}$$

Here the multiplication operators $\mathcal{V}_{\mathrm{ext}}$ and $\mathcal{V}_{\mathrm{H}}$ and the operator $\mathcal{V}_{\mathrm{x}}$ are defined as

$$\phi_k = \phi(x) \longmapsto \mathcal{V}_{\mathrm{ext}}\phi_k = \mathcal{V}_{\mathrm{ext}}\phi_k(x) := V_{\mathrm{ext}}(x)\phi_k(x), \tag{2.15}$$

$$V_{\mathrm{ext}}(x) := \sum_{k=1}^{N_{\mathrm{nuc}}} \frac{Z_k}{|x - X_k|},$$

$$\phi_k = \phi_k(x) \longmapsto \mathcal{V}_{\mathrm{H}}\phi_k = \mathcal{V}_{\mathrm{H}}\phi_k(x) := V_{\mathrm{H}}(x)\phi_k(x),$$

$$V_{\mathrm{H}}(x) := \int \frac{\rho(x')}{|x - x'|}\mathrm{d}x', \tag{2.16}$$

$$\phi_k = \phi_k(x) \longmapsto \mathcal{V}_{\mathrm{x}}\phi_k = \mathcal{V}_{\mathrm{x}}\phi_k(x) := -\int \frac{\rho'(x, x')}{|x - x'|}\phi_k(x')\mathrm{d}x', \tag{2.17}$$

where the *electronic densities* $\rho$ and $\rho'$ are defined as

$$\rho(x) := \sum_{k=1}^{N_{\mathrm{el}}} |\phi_k(x)|^2, \qquad \rho'(x, x') := \sum_{k=1}^{N_{\mathrm{el}}} \phi_k(x)\overline{\phi_k(x')}. \tag{2.18}$$

Here, $V_{\mathrm{H}}$ in (2.16) corresponds to the *classical Hartree integral* [Har28] of the Coulombic electronic interactions, and $\mathcal{V}_{\mathrm{x}}$ in (2.17) defines the *exchange-potential operator*.

The $N_{\mathrm{el}}$-electron problem has thus been mapped onto a set of effective single-particle problems with the *Hartree–Fock potential operator*

$$\mathcal{V}_{\mathrm{HF}} = \mathcal{V}_{\mathrm{ext}} + \mathcal{V}_{\mathrm{H}} + \mathcal{V}_{\mathrm{x}}.$$

Considering the double counting of interactions between electrons $k$ and $\ell$ in $\phi_k^{\mathrm{HF}}$ and $\phi_\ell^{\mathrm{HF}}$, the total energy of the ground state is

$$E_0^{\mathrm{HF}} = \sum_{k=1}^{N_{\mathrm{el}}} \varepsilon_k^{\mathrm{HF}} - \tfrac{1}{2}(E_{\mathrm{H}} + E_{\mathrm{x}}),$$

where

$$E_{\mathrm{H}} := \int \frac{\rho(x)\rho(x')}{|x - x'|}\mathrm{d}x\,\mathrm{d}x', \quad E_{\mathrm{x}} := -\int \frac{\rho'(x, x')\rho'(x', x)}{|x - x'|}\mathrm{d}x\,\mathrm{d}x' \tag{2.19}$$

are the *Hartree* and the *exchange energy*.

In summary, the Hartree–Fock theory assumes that the many-electron wave function $\Phi^{\mathrm{HF}}$ takes the form of a Slater determinant involving single-particle wave functions $\phi_k^{\mathrm{HF}}$. Since the exact wave functions cannot be expressed as single determinants, the problem with this assumption is that Hartree–Fock methods cannot fully represent the solution of the exact many-electron Schrödinger equation (2.6), and the corresponding total energy $E_0^{\mathrm{HF}}$ differs from the true ground-state energy $E_0$. This difference is often referred to as *correlation energy*.

### 2.1.2 Hohenberg–Kohn theorems

With a solution to the $N_{\mathrm{el}}$-electron problem in (2.6), potentially from the Hartree–Fock approximation or some other theory, one can now determine observables from the wave function of the electronic ground state alone. However, the electronic Hamiltonian in (2.5) comprises only one- and two-electron operators: that is, operators that act on either a single electronic coordinate or two. This raises the question, whether it is necessary to look for a solution in terms of an $N_{\mathrm{el}}$-electron wave function after all.

Consider the second-order density matrix, defined as

$$P_2(x_1', x_2'; x_1, x_2) := \binom{N_{\mathrm{el}}}{2} \times \int \Phi(x_1', x_2', \ldots, x_{N_{\mathrm{el}}}) \overline{\Phi(x_1, x_2, \ldots, x_{N_{\mathrm{el}}})}\, \mathrm{d}x_3 \ldots \mathrm{d}x_{N_{\mathrm{el}}}.$$

Its diagonal elements

$$\widetilde{P}_2(x_1, x_2) := P_2(x_1, x_2; x_1, x_2)$$

form the *two-particle density matrix*. A *first-order density matrix* can be written in terms of $P_2$ elements as

$$P_1(x_1'; x_1) := \frac{2}{N_{\mathrm{el}} - 1} \int P_2(x_1', x_2; x_1, x_2) \mathrm{d}x_2,$$

whose diagonal element

$$\widetilde{P}_1(x_1) = P_1(x_1; x_1)$$

is the *charge density*. Instead of using (2.13) to determine the total energy from the full $3N_{\mathrm{el}}$-dimensional wave function $\Phi$, one can obtain

the same via

$$E = \int (\mathcal{T}_{\text{el}} + \mathcal{V}_{\text{nuc-el}})\widetilde{P}_1(x_1)\mathrm{d}x_1 + \iint \mathcal{V}_{\text{el-el}}\widetilde{P}_2(x_1, x_2)\mathrm{d}x_1\mathrm{d}x_2, \quad (2.20)$$

which requires only information about a six-dimensional object. It seems attractive to minimise (2.20) directly by finding optimal density matrices $P_1$ and $P_2$, under the constraint that they are constructible from a proper $\Phi$ that is antisymmetric with respect to exchange of electrons. However, this has in practice not been achieved reliably.

Hohenberg and Kohn realised that one does not even need $\widetilde{P}_2$ to find the ground-state energy, and that it is instead *completely* determined by the charge density $\rho(x) = \widetilde{P}_1(x)$ alone. Two theorems relate the ground state to the electron density:

**Theorem 2.1** (The first Hohenberg–Kohn theorem)**.**

*The density $\rho_0$, which minimises the ground-state energy, uniquely determines the external potential $V_{\text{ext}}$ acting on the electronic system. The ground state $\Phi_0$ is a one-to-one functional of the particle density $\rho$.*
*(Note that in this theorem, external potentials are considered equivalent if they only differ an additional constant which is independent of space.)*

**Theorem 2.2** (The second Hohenberg–Kohn theorem)**.** *The energy functional*

$$E[\rho] = \int V_{\text{ext}}(x)\rho(x)\mathrm{d}x + \int \Phi(\overline{x})\overline{(\mathcal{T}_{\text{el}} + \mathcal{V}_{\text{el-el}})\Phi(\overline{x})}\mathrm{d}\overline{x} \quad (2.21)$$

*obeys a variational principle with respect to the particle density $\rho$ and is minimal for the ground-state density $\rho_0$:*

$$E_0 = E[\rho_0] \leq E[\rho].$$

For proofs of these two theorems, the interested reader is referred to Ref. [HK64]. The above theorems restrict density-functional theory to studies of the ground state.

### 2.1.3 Kohn–Sham theory

From the proofs of the Hohenberg–Kohn theorems, it follows that the exact ground-state energy $E_0$ and density $\rho_0$ can be found by minimising a universal energy functional $E[\rho]$ under the constraint that $\int \rho(x)\mathrm{d}x = N_{\text{el}}$, so

$$\delta\Big\{E[\rho] - \mu\Big[\int \rho(x)\mathrm{d}x - N_{\text{el}}\Big]\Big\} = 0 \quad (2.22)$$

for $\rho = \rho_0$. The Lagrange multiplier $\mu$ can physically be interpreted as a chemical potential. However, the expression of the functional in (2.21) is unsuitable for this purpose, as terms for the kinetic energy and the electron-electron interaction are not expressed as functionals of the density. To work around this problem, Kohn and Sham proposed two approximations. First, they introduced a fictitious system of $N_{\mathrm{el}}$ non-interacting electrons reproducing the exact ground-state density $\rho_0$, described by single-electron wave functions $\phi_k = \phi_k(x)$. They are used to construct an antisymmetric (with respect to electron exchange) $N_{\mathrm{el}}$-electron wave function as a Slater determinant, like in (2.12). For such a system, the kinetic energy is

$$T_{\mathrm{s}}[\rho] = -\tfrac{1}{2}\sum_{k=1}^{N_{\mathrm{el}}} \int \phi_k(x)\overline{\Delta_x \phi_k(x)}\mathrm{d}x \tag{2.23}$$

and the density $\rho$ simply as in (2.18). (Note that since the density $\rho_0$ uniquely determines the external potential (see Theorem 2.1), it also determines all electronic properties of the system, containing the many-body wave function $\Psi$, rendering them, and $T_{\mathrm{s}}$ with them, functionals of $\rho$.) For the electron-electron interaction, one splits off the classical Coulomb interaction, which gives the Hartree energy from (2.19), so that the Kohn–Sham (KS) energy functional reads

$$E^{\mathrm{KS}}[\rho] = T_{\mathrm{s}}[\rho] + \int V_{\mathrm{ext}}(x)\rho(x)\mathrm{d}x + E_{\mathrm{H}}[\rho] + E_{\mathrm{xc}}[\rho]. \tag{2.24}$$

Here, the *exchange-correlation energy functional* $E_{\mathrm{xc}}[\rho]$ combines the differences of the true electron-electron interaction energy $E_{\text{el-el}}$ with all quantum effects and the classical Hartree energy, as well as errors made in the kinetic energy expression:

$$E_{\mathrm{xc}}[\rho] = E_{\text{el-el}}[\rho] - E_{\mathrm{H}}[\rho] + T[\rho] - T_{\mathrm{s}}[\rho].$$

Instead of finding the ground-state energy via variation with respect to the density as in (2.22), one can now perform a variation of (2.24) to find a set of equations to determine the orbitals $\phi_k$ such that the density of the form $\rho$ as in (2.18) minimises $E^{\mathrm{KS}}[\rho]$. This yields a set of effective single-particle equations, known as the *Kohn–Sham equations* [KS65]

$$(-\tfrac{1}{2}\Delta_x + \mathcal{V}_{\mathrm{ext}} + \mathcal{V}_{\mathrm{H}}[\rho] + \mathcal{V}_{\mathrm{xc}}[\rho])\phi_k^{\mathrm{KS}} = \varepsilon_k^{\mathrm{KS}}\phi_k^{\mathrm{KS}}, \tag{2.25}$$

with the effective *Kohn–Sham Hamiltonian*

$$\begin{aligned} H^{\mathrm{KS}} &:= -\tfrac{1}{2}\Delta_x + \mathcal{V}_{\mathrm{KS}}[\rho], \\ \mathcal{V}_{\mathrm{KS}}[\rho] &:= \mathcal{V}_{\mathrm{ext}} + \mathcal{V}_{\mathrm{H}}[\rho] + \mathcal{V}_{\mathrm{xc}}[\rho], \\ f = f(x) &\longmapsto \mathcal{V}_{\mathrm{xc}}[\rho]f = \mathcal{V}_{\mathrm{xc}}[\rho]f(x) := V_{\mathrm{xc}}[\rho](x)f(x), \\ V_{\mathrm{xc}}[\rho] &:= \partial_\rho E_{\mathrm{xc}}[\rho]. \end{aligned} \tag{2.26}$$

Note that $\varepsilon_k^{\mathrm{KS}}$ formally only indicate Lagrangian multipliers, used to introduce the normalising constraints that $\|\phi_k\|_{L^2(\mathbb{R}^3)} = 1$ in the minimisation, but are often interpreted as effective single-particle energies. There is little formal justification to equate them to actual excitations.

Further, there are two points noteworthy about the KS equations (2.25).

First, the variation of the exchange-correlation energy functional $E_{\mathrm{xc}}[\rho]$ with respect to the density $\rho$ defines the *exchange-correlation potential operator* $\mathcal{V}_{\mathrm{xc}}[\rho]$, which is a multiplication operator with the potential function $V_{\mathrm{xc}}[\rho]$ in (2.26). As the exact form of $E_{\mathrm{xc}}[\rho]$ is unknown, one has to resort to physically motivated approximations with varying accuracy. A thorough discussion of specific functional choices is beyond the scope of this work, and we therefore refer the reader to Refs. [Bur12; Mal+14]. Instead, we briefly mention three main types of approximations commonly used among the DFT community. The simplest of these approximations is the *local density approximation* (LDA). The assumption behind this approximation is that the charge density of the system, which is not homogeneous overall, is locally similar to the one of the homogeneous electron gas, whose exchange-correlation energy is known [KS65]. This approximation will be treated more elaborately in the following section. An improvement upon the LDA can be obtained by semi-local Generalised Gradient Approximation (GGA) functionals [Per86a; Per86b]. These depend not just on the value of the density at a point (as in the LDA case), but also on its gradient. The last popular type of approximation is called *hybrid functionals* [LYP88; Bec93]. Hybrid functionals are based on the ansatz that the exact exchange energy is situated between the GGA exchange energy functional and the Hartree–Fock exchange integral. In these, the Hartree–Fock exchange integral is mixed with GGA exchange functionals at a constant ratio.

Second, both the operators $\mathcal{V}_{\mathrm{H}}[\rho]$ and $\mathcal{V}_{\mathrm{xc}}[\rho]$, needed to determine the KS wave functions $\phi_k^{\mathrm{KS}}$, depend on the density $\rho$, which is in turn

determined from the $\phi_k^{\mathrm{KS}}$, requiring a self-consistent procedure to find the solutions in practice.

## 2.2 Time-dependent density-functional theory

An important downside of DFT is, that it is not applicable in the study of time-dependent processes, like chemical reactions, transport phenomena, etc., and photo-excited states. To this end, we need a time-dependent version of the theory and its framework in order to study excitations. A time-dependent formalism has been formulated in the form of Time-Dependent Density-Functional Theory (TDDFT), which has been through a lot of development ever since its beginnings in 1984.

We will formulate TDDFT for a time-dependent version of the system we discussed in Section 2.1, i.e., a spin-unpolarised many-body system of a finite number of $N_{\mathrm{el}}$ electrons, where we consider the nuclear positions $X$ fixed; we will again suppress this parameter as an argument. Nuclear dynamics will be coupled to this treatment of the electronic dynamics later, viz. in the next chapter. In such a system, the time-dependent, full many-body, $N_{\mathrm{el}}$-electron, wave function $\Psi(\overline{x}, t)$ describes the state of the system. Note that in Section 2.1, the state of the time-independent system was described by a time-independent wave function $\Phi = \Phi(\overline{x})$, which satisfies the stationary Schrödinger equation (2.4).

In the time-dependent system, the electrons move in a time-dependent scalar external field, described by the external potential function $V_{\mathrm{ext}} = V_{\mathrm{ext}}(x, t)$. Given $V_{\mathrm{ext}}$ and $N_{\mathrm{el}}$, these quantities constitute the time-dependent Hamiltonian operator

$$H(t) = \mathcal{T}_{\mathrm{el}} + \mathcal{V}_{\text{el-el}} + \mathcal{V}_{\mathrm{ext}}(t), \tag{2.27}$$

and $\Psi$ satisfies the *time-dependent Schrödinger equation*

$$i\partial_t \Psi = H(t)\Psi \tag{2.28}$$

similarly to the time-independent version (2.2). Here, as in the stationary case (2.1), $\mathcal{T}_{\mathrm{el}}$ is the kinetic energy operator, and $\mathcal{V}_{\text{el-el}}$ is the electron-electron interaction, which is assumed to be symmetric and independent of time and spin, and set to the Coulombic interaction potential. Furthermore, the external potential operator

$$\mathcal{V}_{\mathrm{ext}}(t) = \int \mathcal{P} V_{\mathrm{ext}}(x, t) \mathrm{d}x = \sum_{k=1}^{N_{\mathrm{el}}} V_{\mathrm{ext}}(x_k, t) \tag{2.29}$$

denotes the interaction between the electrons and the external field; here, the density operator

$$f = f(x) \longmapsto \mathcal{P}f = \mathcal{P}f(x) := \sum_{k=1}^{N_{\mathrm{el}}} \delta(x - x_j) f(x),$$

with $\delta$ the Dirac delta distribution on $\mathbb{R}^3$. The potential $\mathcal{V}_{\mathrm{ext}}$ can describe, for example, rotational and vibrational excitations in molecules, or the interaction of atoms with external fields, e.g. applied laser fields. Note it couples the time-dependent potential $V_{\mathrm{ext}} = V_{\mathrm{ext}}(x,t)$ to the time-dependent electron density $\rho = \rho(x,t)$, which is defined as

$$\rho(x,t) := N_{\mathrm{el}} \int |\Psi(x, x_2, \ldots, x_{N_{\mathrm{el}}}, t)|^2 \mathrm{d}x_2 \ldots \mathrm{d}x_{N_{\mathrm{el}}}, \tag{2.30}$$

and we see that $\Psi$ defines $\rho$ through integration.

The complete characterisation of the time evolution of our system needs, next to this equation of motion (2.28), the specification of an initial value. Therefore, we specify a state for a time $t = t_0$ as $\Psi(t_0) = \Psi^0$.

This altogether yields an initial-value problem for our time-dependent system, which gives the foundation for the framework for TDDFT, as opposed to the framework for DFT in Section 2.1.

In this section, we will present the basic elements of TDDFT, reminiscent of the foundation we gave for the framework of DFT in Section 2.1. We do this in the following order.

In Section 2.2.1, we will state the theorem by Runge and Gross [RG84], which is the key ingredient providing the formal foundation of TDDFT: in this, we will restrict ourselves to the cases for the Hamiltonian in (2.27). This theorem and its results can be seen as a time-dependent version and extension of the first Hohenberg–Kohn theorem 2.1, given in Section 2.1. This extension the Runge–Gross theorem provides to the time-dependent setting entails, that we can add the following, similar properties to the (time-dependent) system: in short, we show that the density $\rho$ can be used as the fundamental variable in describing quantum many-body systems instead of the time-dependent many-body wave function $\Psi$, and that all properties of the systems are functionals of $\rho$; hence the name.

In Section 2.2.2, we derive the time-dependent Kohn–Sham equations, which can be considered as time-dependent versions of what has

been presented in Section 2.1.3. To do this, we will introduce a quantum-mechanical stationary-action principle and identify such actions in integral form for a fully interacting system and a system consisting of effective non-interacting electrons. There, we also discuss some memory dependence of the exchange-correlation functional, and the approximation we use to tackle this problem, i.e. the time-dependent version of the Local Density Approximation.

### 2.2.1 The Runge–Gross theorem

For the many-body systems we are considering and formulating TDDFT for, the Runge–Gross (RG) theorem can be formulated and applied. As stated, in these systems the time-dependent electronic density $\rho = \rho(x,t)$ changes in response to a time-dependent external scalar potential $V_{\text{ext}} = V_{\text{ext}}(x,t)$, e.g. a time-varying electric field.

The aim of the theorem is to show that for these systems, where the electrons move under the influence of $V_{\text{ext}}$, there exists a one-to-one mapping between the external potential and the electronic density $\rho$ of the system. Since the density uniquely determines the external potential, it also determines all electronic properties of the system, containing the many-body wave function $\Psi$, rendering them functionals of $\rho$. This means that the density $\rho$ can be used as the fundamental variable in describing quantum many-body systems, instead of the time-dependent many-body wave function $\Psi$.

The RG theorem can be considered an analogue of the first Hohenberg–Kohn (HK) theorem 2.1 for time-dependent systems: both establish a mapping between the many-particle state and the corresponding density, and have similar results. Since the reasoning behind the RG theorem differs much from the one behind the HK theorem (for example, there is no general minimisation principle in time-dependent quantum mechanics, by which the proof of the RG theorem is also more involved than the proof of the HK theorem), it is worthwhile to discuss the RG theorem in a more detailed way.

Recall the first HK theorem in Section 2.1.2, which is related to any system consisting of electrons moving under the influence of a time-independent external potential $V_{\text{ext}}$. Note that from this result, we infer that i) time-independent external potentials $V_{\text{ext}} = V_{\text{ext}}(x)$ and time-independent densities $\rho = \rho(x)$ can be written as unique functionals of each other, and ii) if two systems with different time-independent external potentials $V_{\text{ext}}$ and $V'_{\text{ext}}$ give rise to the same time-independent

electronic density $\rho$, their difference is a constant: so, $V'_{\text{ext}} = V_{\text{ext}} + C$.

Similar, time-dependent results follow from the RG theorem: the time-dependent electronic density $\rho = \rho(x,t)$ uniquely determines the time-dependent external potential $V_{\text{ext}} = V_{\text{ext}}(x,t)$, and vice versa, and if two different time-dependent external potentials $V_{\text{ext}}$ and $V'_{\text{ext}}$ give rise to the same time-dependent electronic density $\rho$, their difference is constant in space: $V'_{\text{ext}}(\mathbf{r},t) = V_{\text{ext}}(\mathbf{r},t) + C(t)$.

Note that the aforementioned constant $C$ is for both theorems a constant in space: for the HK theorem, it is also a time-independent constant, while for the RG theorem this is generalised to a time-dependent function $C(t)$, which is constant in space.

Before we move to the RG theorem, it is necessary to study the relation between the time-dependent potentials $V_{\text{ext}}$ and the corresponding time-dependent states $\Psi$ more. It is important to note that we can identify a certain equivalence between different potentials $V_{\text{ext}}$ if they differ by purely time-dependent, additive functions $\partial_t \xi$, constant in space, that are derivatives of scalar and real phase functions $\xi(t)$: in other words,

$$V'_{\text{ext}} \sim V_{\text{ext}} \iff \exists \xi \in C^1(t_0,t) : V'_{\text{ext}}(x,t) = V_{\text{ext}}(x,t) + \partial_t \xi(t). \quad (2.31)$$

Note that this equivalence relation between time-dependent external potentials $V_{\text{ext}}, V'_{\text{ext}}$ gives rise to a certain *phase-transformation invariance*, or a *gauge-transformation invariance* for more general Hamiltonians (see for more information [ED11]) in the following way. The phase functions $\xi$ induce wave functions $\Psi'$, differing only by a phase factor $\exp(-i\xi(t))$ from $\Psi$: so, it only changes the phase of the full wave function $\Psi$ to a phase-transformed state $\Psi'$ by a global time-dependent phase $\xi(t)$ as follows:

$$\Psi'(t) = \exp(-i\xi(t))\Psi(t). \quad (2.32)$$

The additional phase $\xi(t)$ then is absorbed into the gauge-transformed external potential $V'_{\text{ext}}(x,t) = V_{\text{ext}}(x,t) + \partial_t \xi(t)$. We then note that $\Psi'$ satisfies the time-dependent Schrödinger equation

$$i\partial_t \Psi' = \partial_t \xi \exp(i\xi)\Psi + i\partial_t \Psi \exp(-i\xi) = (\mathcal{T}_{\text{el}} + \mathcal{V}_{\text{el-el}} + \mathcal{V}'_{\text{ext}})\Psi', \quad (2.33)$$

with $\Psi$ satisfying (2.28). Now, since the phase $\xi$ is real and constant in space, the phase factor has a unit norm and can be taken out of the integral in (2.30), by which the time-dependent electronic density $n(\mathbf{r},t)$ is *phase-transformation-invariant*: that is, with $\rho'$ being the density originating from $\Psi'$, $\rho' \equiv \rho$.

Note that the constructions above provide a mapping that couples external potentials $V'_{\text{ext}} = V_{\text{ext}} + C$ to identical densities $\rho' = \rho$ via

$$V_{\text{ext}} \longmapsto \Psi \longmapsto \rho, \qquad V'_{\text{ext}} \longmapsto \Psi' \longmapsto \rho. \tag{2.34}$$

Without loss of generality, we assume $\Psi$ and $\Psi'$ to share the initial state $\Psi^0$, rendering the initial-value problems equivalent. Uniqueness of the solution to the time-dependent Schrödinger equation gives us the result, that when $\Psi$ and $\Psi'$ differ by more than just a phase transformation, they can never be induced by equivalent potentials: so, they must stem from two non-equivalent external potentials $V_{\text{ext}} \not\sim V'_{\text{ext}}$. We arrive at a similar result, arguing the other way around: that two wave functions $\Psi$ and $\Psi'$ can never be related by just a phase transformation from two non-equivalent external potentials, even if they share the same initial condition. The proof for this is given in the original formulation of the theorem by Runge and Gross, [RG84] and is based on a *reductio ad absurdum*. The key idea in the proof is, that if (2.33) holds, it must hold that $\mathcal{V}'_{\text{ext}} = \mathcal{V}_{\text{ext}} + \partial_t \xi$, by which it must hold that $V'_{\text{ext}} = V_{\text{ext}} + \partial_t \xi$, which would contradict the non-equivalence that had been assumed.

The theorem is as follows.

**Theorem 2.3** (Runge–Gross, 1984)**.** *[RG84] Given an initial condition on the full wave function $\Psi^0$, the mapping from*

$$\mathscr{V} := \Big\{ V_{\text{ext}} = V_{\text{ext}}(x,t), x \in \mathbb{R}^3, t_0 < t < t_1 \Big| V_{\text{ext}}(x,t) = \\ = \sum_{n=0}^{\infty} \frac{(t-t_0)^n}{n!} \partial_t^n V_{\text{ext}}(x,t_0), \text{ and } \forall V'_{\text{ext}} \in \mathscr{V}, V'_{\text{ext}} \neq V_{\text{ext}} : V_{\text{ext}} \not\sim V'_{\text{ext}} \Big\},$$

*to*

$$\mathscr{N} := \Big\{ \rho = \rho(x,t), x \in \mathbb{R}^3, t_0 < t < t_1 \Big| \rho(x,t) = \\ = N_{\text{el}} \int |\Psi(x, x_2, \ldots, x_{N_{\text{el}}}, t)|^2 \mathrm{d}x_2 \ldots \mathrm{d}x_{N_{\text{el}}}, i\partial_t \Psi = H\Psi \text{ for } V_{\text{ext}} \in \mathscr{V}, \\ \rho(x,t) \xrightarrow{|x| \longrightarrow \infty} 0 \text{ fast enough, for all times } t_0 \leq t \leq t_1 \Big\}.$$

*is one-to-one on any finite time interval $(t_0, t_1)$, $t_1 < \infty$.*

*Proof.* The proof is given in [RG84]. □

This theorem entails that on the time interval $(t_0, t_1)$, the density is a unique functional of the external potential and the initial state, and vice versa: so,

$$\rho = \rho\big[V_{\text{ext}}, \Psi^0\big], \qquad V_{\text{ext}} = V_{\text{ext}}\big[\rho, \Psi^0\big].$$

In short, the set $\mathscr{V}$ is the space of all Taylor-expandable external potentials around $t_0$, modulo solely time-dependent functions, and the set $\mathscr{N}$ is the set of density functions $\rho$ associated with elements $V_{\text{ext}} \in \mathscr{V}$. As we consider only finite systems here, so $N_{\text{el}} < \infty$, we assume that the density vanishes at infinity at all times, faster than the external potentials can increase.

Note that this theorem does not induce a "pure" density-functional method, as it is in general not sufficient to only specify an initial condition for the density $\rho^0$; we really need to know the initial state $\Psi^0$.

For a proof of the RG theorem (and so of the existence of TDDFT) for finite systems and situations in which the Hamiltonian is of the form (2.27), see [Sch+23]. For an extended proof to more general cases, as well as more details, remarks and observations, see [ED11].

### 2.2.2 The time-dependent Kohn–Sham equations

Having established the one-to-one relation between a time-dependent external potentials and time-dependent densities, the next step to think of would be trying to find solutions to the time-dependent Schrödinger equation via a variational principle as we did in the time-independent case, in order to predict the ground-state density. However, in the time-dependent case the situation is too complicated for this, because of the phase factor $\xi$ in the wave functions (see (2.32)), which is almost impossible to determine. Therefore, we seek for a different approach, involving action integrals like the quantum-mechanical action

$$\mathcal{A} := \int_{t_0}^{t_1} \int \Psi(\overline{x}, t)\overline{[i\partial_t - H(t)]\Psi(\overline{x}, t)}\mathrm{d}\overline{x}\mathrm{d}t. \tag{2.35}$$

Variation of the quantum-mechanical action then gives

$$\partial_{\overline{\Psi}}\mathcal{A} = [i\partial_t - H(t)]\Psi(t). \tag{2.36}$$

The stationary states $\Psi$ such that $\partial_{\overline{\Psi}}\mathcal{A} = 0$ are then the solutions of the time-dependent Schrödinger equation (2.2). As stated, these solutions pose a *causality problem*, due to the phase factor $\xi(t)$: this factor allows

for both forward and backward propagation of the wave function in time. This means that as soon as we have obtained a stationary state $\Psi$ for (2.36), it is impossible to determine whether $\Psi$ has evolved forwards from a given initial state $\Psi(t_0)$, or backwards from a given final state $\Psi(t_1)$. This is why the stationary condition (2.36) should be supplemented with a choice for the direction of time. One can find a detailed discussion of how one can account for this in [Mar06].

One can also employ the relation between the density $\rho$ and the wave function $\Psi = \Psi[\rho]$. Using this relation, one can also express the quantum-mechanical action as an *action density functional*

$$\mathcal{A}[\rho] = \underbrace{\int_{t_0}^{t_1} \int \Psi[\rho](\overline{x},t)\overline{[i\partial_t - \mathcal{T}_{\text{el}}]\Psi[\rho](\overline{x},t)}\mathrm{d}\overline{x}\mathrm{d}t}_{\mathcal{A}_0[\rho]}$$
$$- \underbrace{\int_{t_0}^{t_1} \int \Psi[\rho](\overline{x},t)\overline{\mathcal{V}_{\text{el-el}}\Psi[\rho](\overline{x},t)}\mathrm{d}\overline{x}\mathrm{d}t}_{\mathcal{A}_{\text{el-el}}[\rho]} - \underbrace{\int_{t_0}^{t_1} \int \rho(x,t)V_{\text{ext}}(x,t)\mathrm{d}x\mathrm{d}t}_{\mathcal{A}_{\text{ext}}[\rho]} \tag{2.37}$$

with the corresponding stationary condition

$$\partial_\rho \mathcal{A}[\rho] = 0. \tag{2.38}$$

The functional $\mathcal{A}$ is non-local both in space and in time. It depends on all times between $t_0$ and $t_1$ via the density $\rho$ in (2.38). Therefore, it contains *memory effects*: i.e., properties of the system at time $t > t_0$ depend on the way it has evolved from time $t_0$ to $t$.

The *stationary-action principle* can be used to derive a set of time-dependent effective single-particle equations in the TDDFT context, closely resembling the derivation of the Kohn–Sham equations in Section 2.1.3.

To do so, let us write an action integral for an effective non-interacting system, in which the explicit electron-electron interaction is absorbed in an effective potential $V_{\text{eff}} = V_{\text{eff}}(x,t)$, analogous to (2.35), under the assumption that the interacting and effective non-interacting systems produce the same density at $t = t_0$:

$$\mathcal{A}_{\text{eff}}[\rho] := \mathcal{A}_0[\rho] - \int_{t_0}^{t_1} \int \rho(x,t)V_{\text{eff}}(x,t)\mathrm{d}x\mathrm{d}t. \tag{2.39}$$

We rewrite $\mathcal{A}[\rho]$, following the same idea as in Section 2.1.3, by splitting the true quantum internal electronic interactions into a classical Hartree part

$$\mathcal{A}_{\mathrm{H}}[\rho] := \tfrac{1}{2}\int_{t_0}^{t_1}\iint \frac{\rho(x,t)\rho(x',t)}{|x-x'|}\mathrm{d}x'\mathrm{d}x\mathrm{d}t$$

and an exchange-correlation part

$$\widetilde{\mathcal{A}}_{\mathrm{xc}}[\rho] := \mathcal{A}_{\text{el-el}}[\rho] - \mathcal{A}_{\mathrm{H}}[\rho],$$

such that

$$\mathcal{A}[\rho] = \mathcal{A}_0[\rho] - \mathcal{A}_{\mathrm{ext}}[\rho] - \mathcal{A}_{\mathrm{H}}[\rho] - \widetilde{\mathcal{A}}_{\mathrm{xc}}[\rho].$$

With these definitions, it holds that $\mathcal{A}[\rho] = \mathcal{A}_{\mathrm{eff}}[\rho]$, and one can formally write the stationary condition as a variation with respect to $\rho$. Just as in the time-independent setting, this is complicated by the occurrence of the kinetic energy operator $\mathcal{T}_{\mathrm{el}}$ in $\mathcal{A}_0[\rho]$. We resolve this issue by introducing orthonormal, time-dependent single-particle wave functions $\psi_k = \psi_k(x,t)$ producing the exact same time-dependent density of the fully interacting system, given the same initial starting state. Note that the $N_{\mathrm{el}}$-electron wave function $\Psi$ again can be written as a Slater determinant formed by the $\psi_k$, $k = 1,\dots,N_{\mathrm{el}}$. Under this assumption, the density of the system can be written as

$$\rho = \sum_{k=1}^{N_{\mathrm{el}}} |\psi_k|^2. \tag{2.40}$$

In this Kohn–Sham ansatz, one has to account for the difference in the kinetic energies $T_{\mathrm{el}}$ and $T_{\mathrm{s}}$, as in (2.23). This way, we define the *Kohn–Sham action* as

$$\mathcal{A}_{\mathrm{KS}}[\rho] := \mathcal{A}_{0,\mathrm{KS}}[\rho] - \mathcal{A}_{\mathrm{ext}}[\rho] - \mathcal{A}_{\mathrm{H}}[\rho] - \widetilde{\mathcal{A}}_{\mathrm{xc}}[\rho] - (\mathcal{A}_{0,\mathrm{KS}}[\rho] - \mathcal{A}_0[\rho]),$$

with

$$\mathcal{A}_{0,\mathrm{KS}}[\rho] := \sum_{k=1}^{N_{\mathrm{el}}}\int_{t_0}^{t_1}\int \psi_k(x,t)\overline{(i\partial_t + \tfrac{1}{2}\Delta_x)\psi_k(x,t)}\mathrm{d}x\mathrm{d}t$$

and we finally collect all unknown expressions in the *exchange-correlation action functional*

$$\mathcal{A}_{\mathrm{xc}}[\rho] = \mathcal{A}_{\text{el-el}}[\rho] - \mathcal{A}_{\mathrm{H}}[\rho] + \mathcal{A}_{0,\mathrm{KS}}[\rho] - \mathcal{A}_0[\rho].$$

If we now perform the variation of $\mathcal{A}_{\mathrm{KS}}[\rho]$ with respect to the functions $\psi_k$, this leads to the stationary condition

$$\partial_{\overline{\psi_k}} \mathcal{A}_{\mathrm{KS}}[\rho] = (i\partial_t + \tfrac{1}{2}\Delta_x - \mathcal{V}_{\mathrm{KS}}[\rho])\psi_k = 0.$$

Here, we identify the effective potential $V_{\mathrm{eff}}$ in (2.39) with the time-dependent KS potential function $V_{\mathrm{KS}}$, which is defined via the *time-dependent KS potential operator*

$$f = f(x,t) \longmapsto \mathcal{V}_{\mathrm{KS}} f = (\mathcal{V}_{\mathrm{KS}} f)(x,t) := V_{\mathrm{KS}}(x) f(x,t), \tag{2.41}$$

$$V_{\mathrm{KS}}[\rho] := V_{\mathrm{ext}} + V_{\mathrm{H}}[\rho] + V_{\mathrm{xc}}[\rho], \tag{2.42}$$

with the Hartree potential

$$V_{\mathrm{H}}[\rho](x,t) = \int \frac{\rho(x',t)}{|x-x'|} \mathrm{d}x' \tag{2.43}$$

and the exchange-correlation potential

$$V_{\mathrm{xc}}[\rho] = \partial_\rho \mathcal{A}_{\mathrm{xc}}[\rho].$$

So, we conveniently replace the full many-body wave function of the interacting system $\Psi = \Psi(\overline{x}, t)$ by $N_{\mathrm{el}}$ Kohn–Sham single-particle wave functions $\psi_k(x,t)$, satisfying the *time-dependent Kohn–Sham (TDKS) equations*, which are of the form

$$i\partial_t \psi_k = (-\tfrac{1}{2}\Delta_x + \mathcal{V}_{\mathrm{KS}}[\rho])\psi_k, \tag{2.44}$$

and reproducing the exact same electronic density $\rho$ as in the fully interacting case. The only problem with this formulation is that the Kohn–Sham potential function $V_{\mathrm{KS}}[\rho]$ cannot be determined explicitly, due to the unknown expression for the exchange-correlation term. There exist many approximations for the exchange-correlation potential: we will discuss this in Section 3.1.

## 2.3 Mixed quantum-classical dynamics methods

In this section, we present several ways of how to treat nuclear dynamics in a coupled way to the electronic dynamics, for which we derived the time-dependent Kohn–Sham equations. Remember that in the latter procedure, we assumed the nuclei to remain frozen in the ground state.

There are several approaches of how to deal with coupled dynamics. We present the two main methods of the so-called *mixed quantum-classical dynamics* methods. In these methods, we treat the electrons quantum-mechanically in the dynamics, like we did, and the nuclei are treated classically in the dynamics. The two main methods we will discuss are the *surface-hopping* approach and the *mean-field Ehrenfest* approach. For the former one, we only introduce the idea behind it, in order to give an impression of the method; for the latter one, we give a more detailed derivation, since we will choose this method eventually in order to arrive at our system of interest.

### 2.3.1 An overview of mixed quantum-classical dynamics methods

It is simply computationally not feasible to carry out accurate quantum-mechanical calculations of the dynamics of molecular processes involving a large (say, $\mathcal{O}(10)$) number of atoms. There are simplifications to be found in order to tackle this dimensionality problem, in order to arrive at quantum-mechanical solutions, using reduced dimensionality or time-scaling; yet, these simplifications are hard to validate, or even simply not valid.

For a long time, the choice one had to resort to has been molecular dynamics (MD), which is the numerical integration of the classical-mechanical equations governing the motions of atoms on a multi-dimensional potential energy surface. [Tul98b] This method has severe limitations on its own. [AT87] These include practical considerations, like the need for accurate, multidimensional force fields, but also more fundamental ones, related to the underlying theory. The two main approximations conventional MD employs are the *Born–Oppenheimer separation* of electronic and nuclear motion under the assumption that electrons adjust instantaneously to the slower motion of the nuclei, by which the dynamics of the nuclear motion is reduced to a single potential energy surface; [BO27] and the subsequent classical-mechanical treatment of the nuclear motion. This then gives rise to a so-called *adiabatic representation* of the dynamics. However, for a large portion of applications, like electron transfer or photo-induced processes, one or both of these approximations is not valid, as they usually involve more than one potential energy surfaces, with transitions between those energy surfaces: in other words, there is a need for *nonadiabatic representations* of the (coupled) dynamics. These quantised levels require a quantum-mechanical description

of the nuclear motion as well. In order to address this problem, *mixed quantum-classical dynamics methods* have been developed. Here, the objective is to keep a multidimensional classical-mechanical treatment for most of the atoms, whilst selecting a few crucial degrees of freedom to be computed quantum-mechanically.

There are a few issues in using mixed quantum-classical dynamics, which these methods must address correctly. The most important one is *self-consistency*. We have to ensure that the quantum-mechanical degrees of freedom evolve correctly under the influence of the nuclear motion surrounding them. On the other hand, the classical degrees of freedom must correctly respond to the quantum transitions as well. This latter requirement is the most challenging one; there are some standard approach which describe the dynamics of a quantum system interacting with a classical system correctly, like the Redfield approach [Red65; JFF92] and the classical path method [Mot31; Nik74]; but these methods are not able to describe the back reaction of the quantum system on the classical one correctly. This self-consistent interaction is present in the methods that are introduced in the following.

The *surface-hopping method* mostly has been developed in order to introduce classical-quantum correlation, the lack of which is the main drawback of the mean-field Ehrenfest method. This entails that a given trajectory can bifurcate into different branches, each with a particular quantum state and with the amplitude of the state as weights. On the other hand, this method is not as transparent as the mean-field Ehrenfest method, and therefore is prone to misunderstanding: however, it can be shown that this method can be derived from a multi-configuration expansion of the Schrödinger equation using similar approximations as the ones in the mean-field Ehrenfest method. Also, it conserves total energy. Some drawbacks are that the method is not invariant to the choice of quantum representations, and the hopping algorithm is not unique. Further, the accuracy is not as good as the one for the mean-field Ehrenfest method in many applications, and the computational costs are generally higher.

The *mean-field Ehrenfest method*, also called the *eikonal* method, is based on a mean-field separation of the classical and the quantum motion, with a few underlying approximations. It has quite some strong advantages. The underlying approximations are easy to state, and quite clear, which renders this method transparent. Whether the quantum pre-

sentation is adiabatic or non-adiabatic, does not matter to the method: it is invariant to this choice. Also, it ensures a proper conservation of the total energy, so the quantum energy plus the classical energy. One of the drawbacks of this method, like with all mean-field methods, is, that the correlation between the classical and quantum motion is not described.

The derivation of the mean-field Ehrenfest method is discussed in the following. Both methods are discussed in more detail in [Tul98a; Tul98b], [MB07, §2.3], [Ago+13, §V.] and [CB18, §2.1].

### 2.3.2 The mean-field Ehrenfest method

*Note that here in this section, the reduced Planck constant has to be temporarily reintroduced for the derivation of this method, as it is derived performing a classical limit.*

The mean-field Ehrenfest method can be regarded as the classical limit of the *time-dependent self-consistent field method* (TDSCF), or *time-dependent Hartree method*. The TDSCF method is also a mean-field method, meaning it is based on a factorisation of the total wave function into the product of so-called *fast* and *slow* particle parts

$$\Psi(\overline{x}, X, t) = \Xi(\overline{x}, t)\Omega(X, t) \exp\left[\frac{i}{\hbar}\int_0^t E_{\mathrm{q}}(t')\mathrm{d}t'\right]. \tag{2.45}$$

Here, $\Xi$ denotes the wave function to be associated with the 'fast' particle parts, which are identified with the quantum variables (which will be, in our case, the electrons with positions $\overline{x}$); and $\Omega$ denotes the wave function to be associated with the 'slow' particle parts, which are identified with the *to become classical* variables (which will be, in our case, the nuclei with positions $X$). The phase factor $E_{\mathrm{q}}$ is treated below. Both wave functions are normalised for all times $t$: that is,

$$\int \Xi(\overline{x}, t)\mathrm{d}\overline{x} = 1, \qquad \int \Omega(X, t)\mathrm{d}X = 1.$$

We write the Hamiltonian operator for the entire quantum system as

$$H = -\frac{\hbar^2}{2}\sum_{K=1}^{N_{\mathrm{nuc}}}\frac{1}{M_K}\Delta_{X_K} + H_{\mathrm{q}}, \qquad H_{\mathrm{q}}(\overline{x}; X) := -\frac{\hbar^2}{2}\Delta_{\overline{x}} + \mathcal{V}(\overline{x}; X),$$
$$\mathcal{V}(\overline{x}; X) := \mathcal{V}_{\text{nuc-nuc}} + \mathcal{V}_{\text{nuc-el}}(\overline{x}; X) + \mathcal{V}_{\text{el-el}}(\overline{x}).$$

Note that $H_{\mathrm{q}}$, containing all inter-particle interactions, is the Hamiltonian operator of the 'fast' system, with the slow particles fixed at the

positions $X$. The Hamiltonian operator for the 'fast' system then yields the phase factor in (2.45)

$$E_{\mathrm{q}}(t) := \iint \Xi(\overline{x},t)\,\Omega(X,t)\,\overline{H_{\mathrm{q}}(\overline{x};X)\,\Xi(\overline{x},t)\,\Omega(X,t)}\mathrm{d}\overline{x}\mathrm{d}X.$$

We also define the internal phase factors for the two wave functions $\Xi$ and $\Omega$ as

$$E_{\Xi}(t) := i\hbar \int \Xi(\overline{x},t)\,\overline{\partial_t \Xi(\overline{x},t)}\mathrm{d}\overline{x}, \quad E_{\Omega}(t) := i\hbar \int \Omega(X,t)\,\overline{\partial_t \Omega(X,t)}\mathrm{d}X.$$

Note that this choice of phase factors reflects the unequal treatment of 'fast' and 'slow' variables later on. However, phase convention is equivalent to the standard TDSCF approach. We arrive at the following effective Schrödinger equations for the 'fast' and 'slow' variables:

$$i\hbar\partial_t \Xi = -\frac{\hbar^2}{2}\Delta_{\overline{x}}\Xi + \int \Omega(X,t)\,\overline{\mathcal{V}(\overline{x};X)\,\Omega(X,t)}\mathrm{d}X\,\Xi, \tag{2.46}$$

$$i\hbar\partial_t \Omega = -\frac{\hbar^2}{2}\sum_{K=1}^{N_{\mathrm{nuc}}}\frac{1}{M_K}\Delta_{X_K}\Omega + \int \Xi(\overline{x},t)\,\overline{H_{\mathrm{q}}(\overline{x};X)\,\Xi(\overline{x},t)}\mathrm{d}\overline{x}\,\Omega. \tag{2.47}$$

The above equations are at the basis of the mean-field TDSCF method: the 'fast' particles move in the average field of the 'slow' particles, and vice versa. The self-consistent interaction between the 'fast' and 'slow' degrees of freedom in both directions are therefore incorporated.

Now, the Ehrenfest method is obtained by performing a classical limit of (2.47). We follow the procedure stipulated by Messiah, in which the 'slow'-particle wave function $\Omega$ in (2.47) is factorised into an amplitude and a phase term as follows:

$$\Omega(X,t) = \alpha(X,t)\exp\left[\frac{i}{\hbar}S(X,t)\right].$$

The amplitude $\alpha$ and phase $S$ are naturally real-valued. The resulting equations from substitution are, separating the real and imaginary parts,

equivalent to the original Schrödinger equation in (2.47):

$$\partial_t S + \tfrac{1}{2}\sum_{K=1}^{N_{\mathrm{nuc}}} \frac{1}{M_K}|\nabla_{X_K} S|^2 + \int \Xi(\overline{x},t)\,\overline{H_{\mathrm{q}}(\overline{x};X)\,\Xi(\overline{x},t)}\mathrm{d}\overline{x} = \\ = \frac{\hbar^2}{2}\sum_{K=1}^{N_{\mathrm{nuc}}} \frac{1}{M_K}\frac{\Delta_{X_K}\alpha}{\alpha}, \tag{2.48}$$

$$\partial_t \alpha + \sum_{K=1}^{N_{\mathrm{nuc}}} \frac{1}{M_K}(\nabla_{X_K}\alpha\cdot\nabla_{X_K} S + \tfrac{1}{2}\alpha\Delta_{X_K} S) = 0. \tag{2.49}$$

Note that the latter equation (2.49) does not contain $\hbar$. The classical limit is performed using $\hbar \downarrow 0$, which then gives for the former equation (2.48) a right-hand side of zero, yielding the Hamilton–Jacobi equation

$$\partial_t S + \tfrac{1}{2}\sum_{K=1}^{N_{\mathrm{nuc}}} \frac{1}{M_K}|\nabla_{X_K} S|^2 + \int \Xi(\overline{x},t)\,\overline{H_{\mathrm{q}}(\overline{x};X)\,\Xi(\overline{x},t)}\mathrm{d}\overline{x} = 0, \tag{2.50}$$

which is entirely equivalent to the Newton equation, with $p_K = M_K\dot{X}_K$ the classical momentum of particle $K$,

$$\partial_t p_K = -\nabla_{X_K}\Big[\int \Xi(\overline{x},X,t)\,\overline{H_{\mathrm{q}}(\overline{x},X)\,\Xi(\overline{x},X,t)}\mathrm{d}\overline{x}\Big]. \tag{2.51}$$

Now, (2.48) and (2.50) together give a description of a fluid of non-interacting, multidimensional classical particles, so a bunch of independent trajectories, all moving in an average potential of the 'fast' particles. Here, (2.48) describes the continuity of flux. The 'slow' particles now move, using a classical-mechanical description, on a potential energy surface which is given by the expectation value of the 'fast'particle Hamiltonian $H_{\mathrm{q}}$, which gives the mean-field potential. Now, $S$ is the *classical action*

$$S(t) = \int_0^t L(t')\mathrm{d}t',$$

with $L$ the classical Lagrangian, and

$$\dot{X}_K = \frac{1}{M_K}\nabla_{X_K} S.$$

The classical action here consists of the interaction of the electrons with the external, electrostatic potential, and the Coulombic internal nuclear interactions:

$$S[\rho](X) := \int V_{\text{ext}}[X](x)\,\rho(x)\mathrm{d}x + \tfrac{1}{2}\sum_{\substack{K,L=1,\\ L\neq K}}^{N_{\text{nuc}}} \frac{Z_K Z_L}{|X_K - X_L|}. \tag{2.52}$$

Note that the exchange term does not appear in the interaction between the 'fast' (quantum) particles with the 'slow' (classical) ones, as it does not describe electrostatic interaction, but interactions between the electrons.

Note that (2.51) on its down does not complete define the classical limit, as (2.46), the equation defining $\Xi$, still involves $\Omega$. As a usual procedure, $\Omega(X,t)$ is set to $\Omega(X,t) = \delta(X - X(t))$ in (2.46), where $\delta$ is the Dirac delta distribution in $\mathbb{R}^{3N_{\text{nuc}}}$. This gives

$$i\hbar\partial_t \Xi(\overline{x}, X, t) = H_{\text{q}}(\overline{x}, X)\,\Xi(\overline{x}, X, t). \tag{2.53}$$

Now, (2.51) and (2.53) together define the mean-field Ehrenfest method. Note that $\Xi$ now explicitly depends on $X$ as a variable, since it appears explicitly in the equation of motion for the quantum particles, i.e. the electronic variables.

# Chapter 3

# Specifics of the coupled electron-nuclear dynamics under consideration

In this chapter, we discuss the specific choices we make which lead to the eventual system under study. These include a generalisation of the exchange part of the local density approximation for the exchange-correlation potential (so with the correlation part set to zero), discussed in Section 3.1. Together with the electrostatic potential generated by the nuclei as a choice for the external potential, this gives us the eventual class of time-dependent Kohn–Sham equations we will study, discussed in Section 3.2. These equations, describing the electronic dynamics, are coupled to the nuclear equations using the mean-field Ehrenfest method.

In Section 3.3, we discuss the variational formulation and the Hamiltonian structure of our system, with the total energy as a Hamiltonian. Also, conservation of the total energy and electronic charge is shown in this section.

## 3.1 The local-density approximation

As discussed at the end of Sections 2.1.3 and 2.2.2, the only problem with the formulation of both the stationary and the time-dependent Kohn–Sham equations, is that the expression for the exchange-correlation term is unknown. There exist many approximations for the exchange-correlation potential.

The most commonly discussed exchange-correlation potential in the

literature for the Kohn–Sham equations in the time-independent setting is the one using the Local Density Approximation (LDA), introduced by Kohn & Sham in [KS65]. This approximation splits the exchange-correlation potential into exchange and correlation terms $V_{\mathrm{xc}}^{\mathrm{LDA}}[\rho] = V_{\mathrm{x}}^{\mathrm{LDA}}[\rho] + V_{\mathrm{c}}^{\mathrm{LDA}}[\rho]$. Furthermore, it makes the assumption that the exchange part of the energy functional can be approximated by the density of a homogeneous electron gas. [PY89]. This gives for the exchange potential the simple analytic form

$$V_{\mathrm{x}}^{\mathrm{LDA}}[\rho] = -\left(\frac{3}{\pi}\right)^{1/3} \rho^{1/3}. \tag{3.1}$$

For the correlation part, only limiting expressions are known exactly for high and low densities: see e.g. [ED11, §§ 4.3.2, 4.3.3]. Since there are no general analytic expressions known, this leads to a plethora of numerous different approximations; one of the density limits above is taken, or an interpolation between the two (see e.g. [ED11, § 4.3.4]), or the term is parametrised using e.g. density fitting.

In our time-dependent setting, we use the *time-dependent LDA* potential: in this potential, we just replace the stationary density in the LDA exchange-correlation potential $V_{\mathrm{x}}^{\mathrm{LDA}}[\rho]$ by the actual, time-dependent density: see e.g. [ED11, §7.3] This gives

$$V_{\mathrm{xc}}^{\mathrm{TDLDA}}[\rho](t,x) = V_{\mathrm{xc}}^{\mathrm{LDA}}[\rho(t,x)].$$

Due to the absence of a closed form for the correlation potential, and the fact that one in practice has to resort to numerical presentations, which are too complex to investigate in the same manner we handle the other terms (see e.g. [Jer15; AC09]), in this thesis we simply put the correlation part to zero, and we only study a generalisation of the exchange term of the exchange-correlation potential in the (time-dependent) LDA to the form

$$V_{\mathrm{x}}[\rho](t,x) := \lambda \rho(t,x)^{q-1} \tag{3.2}$$

as our exchange potential. In this generalised non-linearity in pure-power form, we introduce the parameters $\lambda \in \mathbb{R}$ and $q > 1$. Note that in the original, time-dependent LDA, the value of $q$ in the exponent is $q = 4/3$, and $\lambda = -(3/\pi)^{1/3}$.

## 3.2 The external potential and the system under consideration

For the external potential, we write the electrostatic potential

$$V_{\mathrm{ext}}[X](x) = -\sum_{K=1}^{N_{\mathrm{nuc}}} \frac{Z_K}{|x - X_K|}, \tag{3.3}$$

which is the external potential generated by the nuclei, corresponding to the Coulombic nucleus-electron interactions. So, $X$ is a parameter here.

Together with our generalisation for the exchange part of the time-dependent LDA (3.1) as a choice for the exchange-correlation potential, this eventually results in the class of time-dependent Kohn–Sham equations we will study, given by

$$i\dot{\psi}_k = -\tfrac{1}{2}\Delta_x\psi_k - \sum_{K=1}^{N_{\mathrm{nuc}}} \frac{Z_K}{|\cdot - X_K|}\psi_k + \left(\frac{1}{|\cdot|} * \rho\right)\psi_k + \lambda\rho^{q-1}\psi_k. \tag{3.4}$$

Note that the mean-field equations (2.53) in the mean-field Ehrenfest method as discussed in Section 2.3.2 are fully equivalent to the time-dependent Kohn–Sham equations for $\hbar \equiv 1$, $\Xi$ acting as the electronic wave function, which is equivalent to $\Psi$ for parametrised $X$, and $H_{\mathrm{q}} = H_{\mathrm{el}}$. In the end, this results in the system

$$i\dot{\psi}_k = -\tfrac{1}{2}\Delta_x\psi_k - \sum_{K=1}^{N_{\mathrm{nuc}}} \frac{Z_K}{|\cdot - X_K|}\psi_k + \left(\frac{1}{|\cdot|} * \rho\right)\psi_k + \lambda\rho^{q-1}\psi_k, \tag{3.5a}$$

$$\ddot{X}_K = \frac{Z_K}{M_K}\left[\int \frac{x - X_K}{|x - X_K|^3}\rho(x)\mathrm{d}x + \sum_{L=1, L\neq K}^{N_{\mathrm{nuc}}} Z_L \frac{X_K - X_L}{|X_K - X_L|^3}\right], \tag{3.5b}$$

with $k \in \{1, \ldots, N_{\mathrm{el}}\}$, $K \in \{1, \ldots, N_{\mathrm{nuc}}\}$, and $\lambda \in \mathbb{R}$, $q > 1$. This coupled system now indicates a class of time-dependent Kohn–Sham equations, in our generalisation for the exchange part of the time-dependent LDA, coupled with Newtonian nuclear dynamics, which describes the nonadiabatic dynamics of a molecular, spin-unpolarised system.

We regard the time-dependent Kohn–Sham equations (3.5a) as evolution equations in the Hilbert space $L^2\big(\mathbb{R}^3; \mathbb{C}^{N_{\mathrm{el}}}\big)$, where the electronic dynamics is governed by the *Kohn–Sham Hamiltonian operator* $H^{\mathrm{KS}}$:

$$\begin{aligned} &i\partial_t\psi = H^{\mathrm{KS}}[X, \rho]\psi, \quad H^{\mathrm{KS}}[X, \rho] = -\tfrac{1}{2}\Delta_x + \mathcal{V}_{\mathrm{KS}}[X, \rho], \\ &\mathcal{V}_{\mathrm{KS}}[X, \rho] = \mathcal{V}_{\mathrm{ext}}[X] + \mathcal{V}_{\mathrm{H}}[\rho] + \mathcal{V}_{\mathrm{x}}[\rho]. \end{aligned} \tag{3.6}$$

where the Kohn–Sham potential $\mathcal{V}_{\mathrm{KS}}$ operator is constituted using the electrostatic potential (3.3) as the external potential $V_{\mathrm{ext}}$ and the exchange part of the local density approximation (3.2) as the exchange potential $V_{\mathrm{x}}$. This indeed gives for $k = 1, \ldots, N_{\mathrm{el}}$

$$(H^{\mathrm{KS}}[X,\rho]\psi)_k = -\tfrac{1}{2}\Delta_x\psi_k - \sum_{K=1}^{N_{\mathrm{nuc}}} \frac{Z_K}{|\cdot - X_K|}\psi_k + \left(\frac{1}{|\cdot|} * \rho\right)\psi_k + \lambda\rho^{q-1}\psi_k. \tag{3.7}$$

The dynamics of the elements $X(t) \in \mathbb{R}^{3N_{\mathrm{nuc}}}$, as described in (3.5b), is driven by the acceleration $A = A^1 + A^2$ as follows:

$$\ddot{X} = A[\rho](X). \tag{3.8}$$

Here, the components of $A$ are defined as

$$\begin{aligned} A^1_K[\rho](X) &:= \frac{Z_K}{M_K}\int \frac{x - X_K}{|x - X_K|^3}\rho(x)\mathrm{d}x, \\ A^2_K(X) &:= \frac{Z_K}{M_K}\sum_{\substack{L=1,\\ L\neq K}}^{N_{\mathrm{nuc}}} Z_L \frac{X_K - X_L}{|X_K - X_L|^3}. \end{aligned} \tag{3.9}$$

In Section 2.3.2, we derived that the nuclei move subject to a single effective potential, corresponding to an average over quantum states:

$$M_K A_K[\rho](X) = -\nabla_{X_K} W[\rho](X), \qquad K = 1, \ldots, N_{\mathrm{nuc}}. \tag{3.10}$$

Using the electrostatic potential, the potential $W$ is of Hellmann–Feynman type:

$$\begin{aligned} W[\rho](X) &:= (V_{\mathrm{ext}}[X], \rho)_{L^2(\mathbb{R}^3)} + W_{\mathrm{nn}}(X), \\ W_{\mathrm{nn}}(X) &:= \tfrac{1}{2}\sum_{\substack{K,L=1,\\ L\neq K}}^{N_{\mathrm{nuc}}} \frac{Z_K Z_L}{|X_K - X_L|}. \end{aligned} \tag{3.11}$$

This potential describes the interaction of the electrons with the external potential, and the Coulombic internal nuclear interactions in $W_{\mathrm{nn}}$. Note that the exchange term does not appear in the coupling of (3.5a) with (3.5b), as it does not describe electrostatic interaction, but interactions between the electrons.

## 3.3 The variational formulation

Note that the equations in our system (3.5) describe a Hamiltonian system, and we can write the system in variational form in the following way.

We define $\mathcal{W} := H^1\big(\mathbb{R}^3;\mathbb{C}^{N_{\mathrm{el}}}\big)\times\mathbb{R}^{6N_{\mathrm{nuc}}}$ with coordinates $(\psi,(X,P))$, and the Hamiltonian $\mathcal{H}:\mathcal{W}\longrightarrow\mathbb{R}$ given by

$$\begin{aligned}\mathcal{H}(\psi,X,P) := {}& \tfrac{1}{2}\sum_{K=1}^{N_{\mathrm{nuc}}}\frac{|P_K|^2}{M_K} + \tfrac{1}{2}\int|\nabla_x\psi(x)|^2\mathrm{d}x - \sum_{K=1}^{N_{\mathrm{nuc}}}Z_K\int\frac{\rho(x)}{|x-X_K|}\mathrm{d}x\\ &+\tfrac{1}{2}\sum_{\substack{K,L=1,\\ L\neq K}}^{N_{\mathrm{nuc}}}\frac{Z_KZ_L}{|X_K-X_L|} + \tfrac{1}{2}\iint\frac{\rho(x)\rho(x')}{|x-x'|}\mathrm{d}x\,\mathrm{d}x' + \frac{\lambda}{q}\int[\rho(x)]^q\mathrm{d}x,\end{aligned} \tag{3.12}$$

where we remember that $\rho=|\psi|^2$. The induced evolution equation is then given in variational form for all $\widetilde{\psi},\widetilde{X},\widetilde{P}$ by

$$\big[\dot\psi,\dot X,\dot P;\widetilde\psi,\widetilde X,\widetilde P\big] = \mathrm{Re}\big\langle D\mathcal{H}\big(\psi,X,P\big),\big(\widetilde\psi,\widetilde X,\widetilde P\big)\big\rangle, \tag{3.13}$$

with the (real-valued) bilinear form

$$\big[\dot\psi,\dot X,\dot P;\widetilde\psi,\widetilde X,\widetilde P\big] := -2\mathrm{Im}\big(\dot\psi,\widetilde\psi\big)_{L^2(\mathbb{R}^3)} - \dot P\cdot\widetilde X + \widetilde P\cdot\dot X$$

and the duality product $\langle\cdot,\cdot\rangle = {}_{\mathcal{W}^*}\langle\cdot,\cdot\rangle_{\mathcal{W}}$.

**Remark 3.1.** Note that in (3.13), the dots indicate *tangent* vectors, which do not need not be actual time derivatives; nevertheless, they will be time derivatives when we derive the system under consideration from this evolution equation. We do this in Appendix B.1.

The Hamiltonian (3.12) is actually the total energy $E$ associated with the system under consideration (3.5). We can write the total energy as

$$E[X,\psi] = E_{\mathrm{kin}}[X,\psi] + W\big[|\psi|^2\big](X) + E_{\mathrm{H}}\big[|\psi|^2\big] + E_{\mathrm{x}}\big[|\psi|^2\big], \tag{3.14}$$

where

$$E_{\mathrm{kin}}[X,\psi] = \tfrac{1}{2}\sum_{K=1}^{N_{\mathrm{nuc}}}M_K\big|\dot X_K\big|^2 + \tfrac{1}{2}\sum_{k=1}^{N_{\mathrm{el}}}\int|\nabla_x\psi_k(x)|^2\mathrm{d}x \tag{3.15}$$

is the total kinetic energy of the system. The other terms are potential energies:

$$E_{\mathrm{H}}\big[|\psi|^2\big] := \tfrac{1}{2}\iint \frac{|\psi(x)|^2|\psi(x')|^2}{|x-x'|}\mathrm{d}x\,\mathrm{d}x' \tag{3.16}$$

is the time-dependent version of the Hartree energy as in (2.19), which in this setting reduces to the electrostatic self-repulsion of the Kohn–Sham electron density. Its variational derivative is calculated as follows.

For any $\phi \in C_{\mathrm{c}}^{\infty}\big(\mathbb{R}^3;\mathbb{C}^{N_{\mathrm{el}}}\big)$, we have

$$\begin{aligned}
&\frac{\partial E_{\mathrm{H}}}{\partial \phi}(\psi) = \frac{\mathrm{d}}{\mathrm{d}t}E_{\mathrm{H}}(\psi+t\phi)\bigg|_{t=0}\\
&= \tfrac{1}{2}\iint \frac{\mathrm{d}}{\mathrm{d}t}\left[\frac{|\psi(x)+t\phi(x)|^2|\psi(x')+t\phi(x')|^2}{|x-x'|}\right]\bigg|_{t=0}\mathrm{d}x\,\mathrm{d}x'\\
&= 2\mathrm{Re}\iint \frac{|\psi(x)|^2\overline{\psi(x')}\phi(x')}{|x-x'|}\mathrm{d}x\,\mathrm{d}x'\\
&= 8\pi\mathrm{Re}\int (-\Delta_x)^{-1}|\psi(x)|^2\overline{\psi(x)}\phi(x)\mathrm{d}x.
\end{aligned}$$

Here, we used that

$$\begin{aligned}
&\frac{\mathrm{d}}{\mathrm{d}t}\big(|\psi(x)+t\phi(x)|^2|\psi(x')+t\phi(x')|^2\big)\bigg|_{t=0}\\
&= |\psi(x)|^2\big[\overline{\psi(x')}\phi(x')+\psi(x')\overline{\phi(x')}\big] + |\psi(x')|^2\big[\overline{\psi(x)}\phi(x)+\psi(x)\overline{\phi(x)}\big]\\
&= A(x,x')+A(x',x),
\end{aligned}$$

with $A(x,x') = 2\mathrm{Re}\big[|\psi(x)|^2\overline{\psi(x')}\phi(x')\big]$, where $\overline{\psi}\phi = \sum_{k=1}^{N_{\mathrm{el}}}\overline{\psi_k}\phi_k$ and $\psi\overline{\phi} = \sum_{k=1}^{N_{\mathrm{el}}}\psi_k\overline{\phi_k}$, with the symmetry $\iint \frac{A(x,x')}{|x-x'|}\mathrm{d}x\,\mathrm{d}x' = \iint \frac{A(x',x)}{|x-x'|}\mathrm{d}x\,\mathrm{d}x'$, and the fact that

$$u(x) = \int \frac{|\psi(x')|^2}{|x-x'|}\mathrm{d}x',$$

as it solves $-\Delta_x u = 4\pi|\psi|^2$, can be written as $u = 4\pi(-\Delta_x)^{-1}|\psi|^2$.

Furthermore,

$$E_{\mathrm{x}}\big[|\psi|^2\big] := \frac{\lambda}{q}\int |\psi(x)|^{2q}\mathrm{d}x \tag{3.17}$$

is the exchange energy, of which the variational derivative is calculated as follows.

For any $\phi \in C_c^\infty\big(\mathbb{R}^3;\mathbb{C}^{N_{\mathrm{el}}}\big)$, we have

$$\begin{aligned}\frac{\partial E_{\mathrm{x}}}{\partial \phi}(\psi) &= \frac{\mathrm{d}}{\mathrm{d}t}E_{\mathrm{x}}(\psi+t\phi)\Big|_{t=0} = \frac{\lambda}{q}\int \frac{\mathrm{d}}{\mathrm{d}t}\Big[\big(|\psi(x)+t\phi(x)|^2\big)^q\Big]\Big|_{t=0}\mathrm{d}x\\ &= \lambda\int \big(|\psi(x)+t\phi(x)|^2\big)^{q-1}\Big|_{t=0}\frac{\mathrm{d}}{\mathrm{d}t}\big(|\psi(x)+t\phi(x)|^2\big)\Big|_{t=0}\mathrm{d}x\\ &= 2\lambda\mathrm{Re}\int |\psi(x)|^{2(q-1)}\overline{\psi(x)}\phi(x)\mathrm{d}x,\end{aligned}$$

as

$$\begin{aligned}&\frac{\mathrm{d}}{\mathrm{d}t}\big(|\psi+t\phi|^2\big)\Big|_{t=0} = \frac{\mathrm{d}}{\mathrm{d}t}\big[|\psi|^2+t\big(\overline{\psi}\phi+\psi\overline{\phi}\big)+t^2|\phi|^2\big]\Big|_{t=0}\\ &= \overline{\psi}\phi+\psi\overline{\phi} = 2\mathrm{Re}\overline{\psi}\phi.\end{aligned}$$

The total energy $E$ as well as the electron charge $\|\psi\|_{L^2}^2$ are conserved under the dynamics, as one can expect due to the time and gauge invariances of our system. In what follows, we use the notion of *self-adjointness*. We define this property as is done in [GS03, Defn. 2.4].

**Definition 3.2** ([GS03])**.** A linear operator $A$ on $L^2(\mathbb{R}^3)$ is self-adjoint if

- $A$ is symmetric: i.e., $(\psi_1, A\psi_2)_{L^2(\mathbb{R}^3)} = (A\psi_1,\psi_2)_{L^2(\mathbb{R}^3)}$ for all $\psi_1,\psi_2 \in L^2(\mathbb{R}^3)$, and
- the equations $(A \pm i)\psi = f$ have solutions for all $f \in L^2(\mathbb{R}^3)$.

With this notion, we can prove the following lemma.

**Lemma 3.3.** *Let $T > 0$ be arbitrary, and let the pair*

$$\begin{aligned}&\psi \in C^0\big([0,T];H^2\big(\mathbb{R}^3;\mathbb{C}^{N_{\mathrm{el}}}\big)\big)\cap C^1\big([0,T];L^2\big(\mathbb{R}^3;\mathbb{C}^{N_{\mathrm{el}}}\big)\big)\\ &X \in C^2\big([0,T];\mathbb{R}^{3N_{\mathrm{nuc}}}\big)\end{aligned}$$

*be any solution of the system (3.5). Then, the following results hold. The total energy $E[X,\psi]$ as well as the electron charge $\|\psi\|_{L^2}^2$ are conserved quantities in time on $[0,T)$.*

*Proof. Conservation of total charge.*
On $[0,T)$, for $\psi$ solving (3.5a),

$$\frac{\mathrm{d}}{\mathrm{d}t}\big(\|\psi\|_{L^2}^2\big) = (-iH^{\mathrm{KS}}[X,\rho]\psi,\psi)_{L^2} + (\psi,-iH^{\mathrm{KS}}[X,\rho]\psi)_{L^2} = 0,$$

since for the given solution $(\psi, X)$, the time-dependent operator $H^{\mathrm{KS}}[X,\rho]$ is a self-adjoint operator on $L^2$ on $[0,T)$; see also Definition 3.2. By this, the electron charge is conserved in time on $[0,T)$.

*Conservation of total energy.*
By density, on $[0,T)$

$$\tfrac{1}{2}\frac{\mathrm{d}}{\mathrm{d}t}\Big(\int |\nabla_x\psi(x)|^2\mathrm{d}x\Big) = 2\mathrm{Re}\big(-\tfrac{1}{2}\Delta_x\psi,\dot\psi\big)_{L^2}.$$

Furthermore, on $[0,T)$

$$\begin{aligned}
\frac{\mathrm{d}W}{\mathrm{d}t} &= \frac{\mathrm{d}}{\mathrm{d}t}\Big[-\sum_{K=1}^{N_{\mathrm{nuc}}}\int\frac{Z_K}{|x-X_K|}\rho(x)\mathrm{d}x + \tfrac{1}{2}\sum_{K=1}^{N_{\mathrm{nuc}}}\sum_{L=1,L\neq K}^{N_{\mathrm{nuc}}}\frac{Z_KZ_L}{|X_K-X_L|}\Big]\\
&= \sum_{L'=1}^{N_{\mathrm{nuc}}}\nabla_{X_{L'}}\Big[-\sum_{K=1}^{N_{\mathrm{nuc}}}\int\frac{Z_K}{|x-X_K|}\rho(x)\mathrm{d}x + \tfrac{1}{2}\sum_{K=1}^{N_{\mathrm{nuc}}}\sum_{L=1,L\neq K}^{N_{\mathrm{nuc}}}\frac{Z_KZ_L}{|X_K-X_L|}\Big]\cdot\\
&\qquad\cdot\dot X_{L'} - 2\sum_{K=1}^{N_{\mathrm{nuc}}}\int\frac{Z_K}{|x-X_K|}\mathrm{Re}\Big[\psi(x)\cdot\overline{\dot\psi(x)}\Big]\mathrm{d}x\\
&= -\sum_{K=1}^{N_{\mathrm{nuc}}}M_K\ddot X_K\cdot\dot X_K + 2\mathrm{Re}\Big(-\sum_{K=1}^{N_{\mathrm{nuc}}}\frac{Z_K}{|x-X_K|}\psi,\dot\psi\Big)_{L^2},
\end{aligned}$$

by the chain rule, and

$$\begin{aligned}
\frac{\mathrm{d}E_{\mathrm{H}}}{\mathrm{d}t} &= \tfrac{1}{2}\frac{\mathrm{d}}{\mathrm{d}t}\Big[\iint\frac{\rho(x)\rho(x')}{|x-x'|}\mathrm{d}x\,\mathrm{d}x'\Big]\\
&= \iint\frac{1}{|x-x'|}\Big\{\mathrm{Re}\Big[\psi(x)\cdot\overline{\dot\psi(x)}\Big]\rho(x') + \rho(x)\mathrm{Re}\Big[\psi(x')\cdot\overline{\dot\psi(x')}\Big]\Big\}\mathrm{d}x\,\mathrm{d}x'\\
&= 2\mathrm{Re}\Big[\Big(\int\frac{\rho(x')}{|\cdot-x'|}\mathrm{d}x'\psi,\dot\psi\Big)_{L^2}\Big]
\end{aligned}$$

by symmetry. Also,

$$\frac{\mathrm{d}E_{\mathrm{x}}}{\mathrm{d}t} = \frac{\lambda}{q}\frac{\mathrm{d}}{\mathrm{d}t}\Big[\int\rho(x)^q\mathrm{d}x\Big] = 2\mathrm{Re}\big[\big(\lambda\rho^{q-1}\psi,\dot\psi\big)_{L^2}\big], \tag{3.18}$$

which is finite for all $q>1$ since $H^2(\mathbb{R}^3)$ is embedded into all Lebesgue spaces $L^r$, $2\le r\le\infty$.

Combining the results above, we get on $[0,T)$

$$\frac{\mathrm{d}}{\mathrm{d}t}E[X,\psi] = 2\mathrm{Re}\big(H^{\mathrm{KS}}[X,\rho]\psi,\dot\psi\big)_{L^2} = -2\mathrm{Re}\big(i\|\dot\psi\|_{L^2}^2\big) = 0.$$

By this, the total energy is conserved in time on $[0,T)$. □

# Chapter 4

# Well-posedness results for $q \geq 7/2$ in $H^2$

In this chapter, we prove short-time existence and uniqueness of solutions of the initial-value problem associated with the system

$$i\dot{\psi}_k = -\tfrac{1}{2}\Delta_x\psi_k - \sum_{K=1}^{N_{\mathrm{nuc}}} \frac{Z_K}{|\cdot - X_K|}\psi_k + \left(\frac{1}{|\cdot|} * \rho\right)\psi_k + \lambda\rho^{q-1}\psi_k, \quad (4.1a)$$

$$\ddot{X}_K = \frac{Z_K}{M_K}\left[\int \frac{x - X_K}{|x - X_K|^3}\rho(x)\mathrm{d}x + \sum_{L=1, L\neq K}^{N_{\mathrm{nuc}}} Z_L \frac{X_K - X_L}{|X_K - X_L|^3}\right]. \quad (4.1b)$$

We do this by combining Yajima's theory for time-dependent, linear Hamiltonians with Duhamel's principle based on suitable Lipschitz estimates for the non-linear part of our Hamiltonian. We identify a range of exponents $q$ in the pure-power exchange term within the generalisation of the local density approximation, for which there exist unique solutions on a certain time interval to (4.1) in a function space involving the Sobolev space $H^2(\mathbb{R}^3)$ as setting for the Kohn–Sham wave functions $\psi_k$.

We use the shorthand notation

$$\psi = (\psi_1, \ldots, \psi_{N_{\mathrm{el}}}) : t \longmapsto H^2\big(\mathbb{R}^3; \mathbb{C}^{N_{\mathrm{el}}}\big).$$

The main result of this chapter is the following.

**Theorem 4.1.** *Let $q \geq 7/2$ and $\lambda \in \mathbb{R}$. Let $\psi^0 \in H^2\big(\mathbb{R}^3; \mathbb{C}^{N_{\mathrm{el}}}\big)$, $V^0 \in \mathbb{R}^{3N_{\mathrm{nuc}}}$ and $X^0 \in \mathbb{R}^{3N_{\mathrm{nuc}}}$ be given, with $X^0_K \neq X^0_L$ for $K \neq L$.*

*Then there exists $\tau > 0$ such that the initial-value problem associated with the system (4.1) with $\psi(t) = \psi^0$, $X(0) = X^0$ and $\dot{X}(0) = V^0$ has a*

*unique solution* $(\psi, X)$ *in the function space*

$$C^0\big([0,\tau];H^2\big(\mathbb{R}^3;\mathbb{C}^{N_{\mathrm{el}}}\big)\big)\cap C^1\big([0,\tau];L^2\big(\mathbb{R}^3;\mathbb{C}^{N_{\mathrm{el}}}\big)\big)\times C^2\big([0,\tau];\mathbb{R}^{3N_{\mathrm{nuc}}}\big).$$

In Section 4.1, we recall relevant results from evolution-operator theory, especially from Kenji Yajima's article [Yaj87] on the construction and properties of a family of evolution operators associated with linear Hamiltonians.

In Section 4.2, we give a short literature review on previous results by other authors on similar coupled evolution equations, in particular some results by Cancès & Le Bris [CB99], such as bounds on the operator norms of these evolution operators associated with linear Hamiltonians.

In the later sections, we give a proof of Theorem 4.1.

First, in Section 4.3, we state some preliminary results.

In Sections 4.4 we define bounded regions that are designed to seek solutions of the subsystems (4.1a) and (4.1b) on the time interval $[0,\tau]$, as well as mappings which connect these solutions.

In Section 4.5, in view of a Duhamel-type argument developed in later sections, we state and prove some Lipschitz estimates on the nonlinear terms at the right-hand side of (4.1a). The restriction $q \geq 7/2$ arises from these estimates.

Next, we prove in Sections 4.6 and 4.7 that for some $\tau > 0$ and $q \geq 7/2$, for fixed electronic and nuclear configurations as elements of the bounded regions, the separate subsystems describing the nuclear resp. electronic dynamics have unique solutions, and the mappings connecting the solutions are is bounded and continuous with respect to the topologies the bounded regions are employed with. We construct these solutions as fixed points of certain mappings, and argue using preliminary results, the Lipschitz estimates and Yajima's theory on evolution operators that these fixed points are strong solutions of the subsystems.

After this, we prove in Section 4.8 that for $q \geq 7/2$ and some $\tau > 0$, the initial-value problem associated to the problem (4.1) has a solution $(\psi, X)$ in

$$C^1\big([0,\tau];L^2\big(\mathbb{R}^3;\mathbb{C}^{N_{\mathrm{el}}}\big)\big)\cap C^0\big([0,\tau];H^2\big(\mathbb{R}^3;\mathbb{C}^{N_{\mathrm{el}}}\big)\big)\times C^2\big([0,\tau];\mathbb{R}^{3N_{\mathrm{nuc}}}\big).$$

To this end, we construct a concatenation of the mappings defined before, to which we apply a Schauder-type argument in the spirit of [CB99]. Unlike in [CB99], we equip $\mathcal{B}_{\mathrm{nuc}}(\tau)$ with a weaker $C^0$ topology, which

takes into account nuclear repulsion. In the same section, we prove uniqueness of the solution $(\psi, X)$. To this end, we use results on Lorentz spaces; see also Section A.2. Note that the whole of Appendix A is dedicated to the notation we systematically use, comprising the norms on the various functional spaces we use, as $H^2$ and Lorentz spaces.

## 4.1 Evolution-operator theory

In this section, we lay out the connection of the dynamics of our system to *evolution operators*, or *propagators*. Using these operators, we formulate statements on existence of solutions of Schrödinger-type equations.

The *free propagator* is the operator family $\{U_0(t), t \in \mathbb{R}\}$ containing the evolution operators associated to the free particle: this situation is described by Schrödinger's equation in the absence of a potential: that is, $\mathcal{V} \equiv 0$. The free propagator is then written as

$$U_0(t) = e^{\frac{it}{2}\Delta_x}.$$

Note that it forms a strongly continuous semigroup.

**Definition 4.2.** A *strongly continuous semigroup* on a Banach space $B$ is a map $S : \mathbb{R}_+ \longrightarrow \mathcal{L}(B)$ such that

1. $S(0) = \mathrm{Id}$, which is the identity operator on $B$;
2. $S(t+s) = S(t)S(s)$ for all $t, s \geq 0$;
3. for all $f \in B$, $\|S(t)f - f\|_B \longrightarrow 0$ as $t \downarrow 0$.

The last property states that the map defined by $S$ is continuous in the strong operator topology.

It is possible to derive how the operators $U_0(t)$ act on $L^2(\mathbb{R}^3)$ (or general dimensions $n \in \mathbb{N}$, for that matter) explicitly: using Fourier transforms on $L^2(\mathbb{R}^3)$,

$$U_0(t)\psi = (it)^{-3/2} e^{\frac{i|\cdot|^2}{2t}} \mathcal{F}\left[e^{\frac{i|\cdot|^2}{2t}}\psi\right]\left(\frac{\cdot}{t}\right) = (2\pi i|t|)^{-3/2} \int e^{\frac{i|\cdot - x|^2}{2t}} \psi(x) \mathrm{d}x. \tag{4.2}$$

Estimates using the free propagator are widely used in the study of time-dependent evolution equations like the time-dependent Schrödinger-type equation. In [Kat70], Tosio Kato proved the following Lemma.

**Lemma 4.3.** *Let $m \in [2, \infty]$ and $m' = \frac{m}{m-1}$ its dual exponent. Then, we have the following. For all $f \in L^{m'}(\mathbb{R}^3)$,*

$$U_0(t)f \in C^0(\mathbb{R} \setminus \{0\}; L^m(\mathbb{R}^3)),$$

*with*

$$\|U_0(t)f\|_{L^m(\mathbb{R}^3)} \leq \frac{1}{(2\pi|t|)^{3/2-3/m}} \|f\|_{L^{m'}(\mathbb{R}^3)}.$$

*Proof.* This follows directly from applying Young's convolution inequality (A.6) to (4.2). □

The above inequality is widely used in the scattering theory for Schrödinger equations: see e.g. [How74]. We will use it later as a smoothing property of the free propagator.

In [Yaj87], Yajima investigates the existence, uniqueness and regularity of the solution to the time-dependent Schrödinger equation on $\mathbb{R}^n$, for general spatial dimensions $n \in \mathbb{N}$. We restrict ourselves to $n = 3$:

$$\begin{aligned} i\partial_t \psi(t,x) &= -\tfrac{1}{2}\Delta_x \psi(t,x) + V(t,x)\psi(t,x) \text{ for } (t,x) \in I_\Theta \times \mathbb{R}^3, \\ \psi(s,x) &= \psi^0(x) \text{ on } \mathbb{R}^3, \end{aligned}$$

with the time domain $I_\Theta := [-\Theta, \Theta]$, and $-\Theta < s < \Theta$. Furthermore, $V$ is again assumed to be a real-valued function, and we can consider this as an evolution equation on the Hilbert space $L^2(\mathbb{R}^3)$:

$$i\partial_t \psi = H(t)\psi, \qquad H(t) = -\tfrac{1}{2}\Delta_x + \mathcal{V}(t), \qquad \psi(s) = \psi^0, \tag{4.3}$$

with $\mathcal{V}(t)$ on $L^2(\mathbb{R}^3)$ defined as $\psi = \psi(t,x) \longmapsto \mathcal{V}(t)\psi = V(t,x)\psi(t,x)$.

Using perturbation techniques and Lebesgue-space estimates for the free propagator $U_0(t) = \exp(it\Delta_x/2)$, sufficient conditions are sought for the potential function $V(t,x)$, such that

- the time-dependent Schrödinger equation (4.3) generates a unique, strongly continuous unitary propagator $\{U(t,s), t, s \in I_\Theta\}$ on $L^2(\mathbb{R}^3)$ (which is a two-parameter group, as both $t$ and $s$ (for the initial condition) are involved as parameters), and
- for the unique solution $\psi(t) = U(t,s)\psi^0$ to (4.3), it holds that

  $$U(t,s)\psi^0 \in C^0\big(I_\Theta; H^2(\mathbb{R}^3)\big) \cap C^1\big(I_\Theta; L^2(\mathbb{R}^3)\big)$$

  for all $\psi^0 \in H^2(\mathbb{R}^3)$.

The conditions for $V$ will be sufficient to allow for moving singularities in $V$ of the type $|x|^{\varepsilon-3/2}$, where $\varepsilon > 0$.

Another concept in the study of time-dependent evolution equations is *Duhamel's principle*, by which the solution to (4.3) can be given by the integral equation

$$\psi(t) = U_0(t-s)\psi^0 - i\int_s^t U_0(t-t')\mathcal{V}(t')\psi(t')\mathrm{d}t'. \tag{4.4}$$

Also, we consider the Bochner spaces

$$L^{m,\rho}(I) := L^\rho\big(I; L^m(\mathbb{R}^3)\big),$$

for an interval $I$ and coefficients $m, \rho \in [1, \infty)$. These can be considered 'composite Lebesgue spaces', and are equipped with the norm

$$\|f\|_{L^{m,\rho}(I)} = \bigg\{ \int_I \Big[ \int |f(t,x)|^m \mathrm{d}x \Big]^{\rho/m} \mathrm{d}t \bigg\}^{1/\rho}.$$

We formulate the following assumption on the potential function $V$.

**Assumption 4.4.** There exist $p \geq 1$, $\alpha \geq 1$, and $\beta > 1$, with

$$0 \leq \frac{1}{\alpha} < 1 - \frac{3}{2p},$$

such that we have

$$V \in L^{p,\alpha}(I_\Theta) + L^{\infty,\beta}(I_\Theta). \tag{4.5}$$

Note that the plus sign indicates the direct sum of two vector spaces: see also Section A.1. This means that there exist $V_1 \in L^{p,\alpha}(I_\Theta)$ and $V_2 \in L^{\infty,\beta}(I_\Theta)$ such that $V = V_1 + V_2$ for almost every $t \in I_\Theta, x \in \mathbb{R}^3$.

We set

$$\theta(\ell) := \frac{2}{3\Big(\frac{1}{2} - \frac{1}{\ell}\Big)}.$$

for $2 \leq \ell \leq \infty$ (note that $\theta(2) = \infty$ and $\theta(\infty) = 4/3$), and

$$q^* := \frac{2p}{p-1}, \tag{4.6}$$

with $p$ as in Assumption 4.4. Note that $\theta(q^*) = 4p/3$.

**Theorem 4.5.** *Under Assumption 4.4, we have the following results.*

1. *For all $\psi^0 \in L^2(\mathbb{R}^3)$, equation (4.4) has a unique solution*
$$\psi \in C^0\big(I_\Theta, L^2(\mathbb{R}^3)\big) \cap L^{q^*,4p/3}(I_\Theta).$$
2. *For all $t \in I_\Theta$*
$$\|\psi(t)\|_{L^2(\mathbb{R}^3)} = \big\|\psi^0\big\|_{L^2(\mathbb{R}^3)}.$$

**Corollary 4.6.** *There exists a unique family of unitary operators*
$$\{U(t,s), t, s \in I_\Theta\}$$
*on $L^2(\mathbb{R}^3)$ such that*

1. *$U(t,s)U(s,r) = U(t,r)$ for all $t, s, r \in I_\Theta$,*
2. *$U(t,t) = \mathrm{Id}$ for all $t \in I_\Theta$,*
3. *for all $f \in L^2(\mathbb{R}^3)$, the mapping $(t,s) \longmapsto U(t,s)f$ is continuous from $I_\Theta^2$ to $L^2(\mathbb{R}^3)$,*
4. *for all $f \in L^2(\mathbb{R}^3)$, we have that*
$$\|U(t,s)f\|_{L^{q,4p/3}(I_\Theta)} \le C_{q,\Theta}\|f\|_{L^2(\mathbb{R}^3)}$$
5. *$\psi(t) = U(t,s)\psi^0$ solves (4.4) for all $\psi^0 \in L^2(\mathbb{R}^3)$.*

Note these unitary operators also define a strongly continuous semigroup; see Definition 3.2.

For the case that $p \ge 2$, Assumption 4.4 implies that the operators $H(t)$, $t \in I_\Theta$, are self-adjoint on $L^2(\mathbb{R}^3)$, with domain $H^2(\mathbb{R}^3)$ and $C_0^\infty$ as its core (cf. [RS75, Thm. X.29 ff.]). Then, the solution $\psi(t) = U(t,s)\psi^0$ solves (4.3) in $H^{-2}(\mathbb{R}^3)$ almost everywhere.

We formulate a condition on $V$ such that we are able to establish a result of similar nature in the space $H^2(\mathbb{R}^3)$.

**Assumption 4.7.** We assume that
$$V \in L^{\infty,\widetilde{p}}(I_\Theta) + L^{\infty,\infty}(I_\Theta), \qquad \partial_t V \in L^{p_1,\alpha_1}(I_\Theta) + L^{\infty,\beta}(I_\Theta).$$
Here, $\widetilde{p} := \max\{p, 2\}$, $p_1 = \frac{2p}{p+1}$, and $\alpha_1 > \frac{4p}{4p-3}$. In these parameters, Further, here $\beta$ and $p$ are taken as in Assumption 4.4.

Note that Assumption 4.7 implies Assumption 4.4.

**Theorem 4.8.** *Under Assumption 4.7, the strongly continuous, unitary propagator $\{U(t,s), t,s \in I_\Theta\}$ satisfies the properties (1)–(5). Furthermore, it satisfies the following additional properties:*

6. *$U(t,s) \in \mathcal{L}\big(H^2(\mathbb{R}^3)\big)$ for all $t,s \in I_\Theta$,*
7. *For all $f \in H^2(\mathbb{R}^3)$, the mapping $(t,s) \longmapsto U(t,s)f$ is continuous on $I_\Theta^2$ with values in $H^2(\mathbb{R}^3)$,*
8. *For all $f \in H^2(\mathbb{R}^3)$, we have that the mapping $(t,s) \longmapsto U(t,s)f$ is an element of $C^1\big(I_\Theta^2; L^2(\mathbb{R}^3)\big)$, and the following equations hold in $L^2(\mathbb{R}^3)$:*

$$i\partial_t U(t,s)f = H(t)U(t,s)f,$$
$$i\partial_s U(t,s)f = -U(t,s)H(s)f.$$

9. *For all $\psi^0 \in H^2(\mathbb{R}^3)$ and $s \in I_\Theta$,*

$$\partial_t U(t,s)\psi^0 \in C^0\big(I_\Theta; L^2(\mathbb{R}^3)\big) \cap L^{q^*,4p/3}(I_\Theta).$$

*Moreover, a family $\{U(t,s), t,s \in I_\Theta\}$ satisfying properties (1)–(3) and (6)–(8) is unique.*

Here, $\mathcal{L}(B,B')$ denotes the space of all linear operators $A : B \longrightarrow B'$ for Banach spaces $B, B'$. We write $\mathcal{L}(B,B) = \mathcal{L}(B)$. See also A.1.

The proofs for all results in this section can be found in [Yaj87]. However, we will later on use some ideas of this proof, which we outline here.

For a time-independent Schrödinger operator $H$, we use that it is self-adjoint, and Stone's theorem on strongly continuous one-parameter unitary semigroups (see e.g. [Hal13, Theorem 10.15] gives the unitary group of operators

$$U(t,s) = e^{-i(t-s)H}, t,s \in I_\Theta,$$

which satisfies properties (1–3) and (5–8), under Assumption 4.7.

However, if we consider general time-dependent Schrödinger operators $H(t)$, existence theorems as [Kat73, Theorem 1] cannot easily be

applied, as the conditions on the potential $V(t,x)$ are too rigorous, by which even general Coulomb potentials of the form $V(x) \sim |x|^{-1}$ would be excluded. Thus, we have to refine Kato's theory to include at least the natural, basic potentials we encounter everywhere. To this end, we will use the smoothing property of the free propagator $U_0$, together with a consequence of Kato's inequality as given in Lemma 4.3. This inequality has been used before to prove the existence of the unitary propagator for the time-dependent Schrödinger equation with a singular potential $V(t,x)$ in a different setting: see [How74]. In a broader sense of the study on non-linear Schrödinger equation, it has proven to be of vital use: see e.g. [Kat87].

For the results, we use the integral operators involving the free propagator

$$(S\psi)(t) := \int_0^t U_0(t-t')\psi(t')\mathrm{d}t', \qquad (Q\psi)(t) := (SV\psi)(t),$$

and the Banach spaces over $I_a \times \mathbb{R}^3$ for $\ell \in [2,\infty]$ such that $\theta(\ell) \in (2,\infty]$, where $\ell' = \frac{\ell}{\ell-1}, \theta(\ell)' = \frac{\theta(\ell)}{\theta(\ell)-1}$ indicate dual exponents:

$$\begin{aligned}
\mathscr{X}(a,\ell) &:= L^{2,\infty}(I_a) \cap L^{\ell,\theta(\ell)}(I_a),\\
\mathscr{X}^*(a,\ell) &:= L^{2,1}(I_a) + L^{\ell',(\theta(\ell))'}(I_a),\\
\mathscr{Y}(a,\ell) &:= \big\{\psi \in L^\infty\big(I_a; H^2(\mathbb{R}^3)\big) \big| \dot\psi \in \mathscr{X}(a,\ell)\big\},\\
\mathscr{Y}^*(a,\ell) &:= \big\{\psi \in L^{2,\infty}(I_a) \big| \dot\psi \in \mathscr{X}^*(a,\ell)\big\},
\end{aligned}$$

equipped with the norms

$$\begin{aligned}
\|\psi\|_{\mathscr{X}(a,\ell)} &= \|\psi\|_{L^{2,\infty}(I_a)} + \|\psi\|_{L^{\ell,\theta(\ell)}(I_a)},\\
\|\psi\|_{\mathscr{X}^*(a,\ell)} &= \|\psi\|_{L^{2,1}(I_a)+L^{\ell',(\theta(\ell))'}(I_a)},\\
\|\psi\|_{\mathscr{Y}(a,\ell)} &= \|\psi\|_{L^\infty\left(I_a;H^2(\mathbb{R}^3)\right)} + \big\|\dot\psi\big\|_{\mathscr{X}(a,\ell)},\\
\|\psi\|_{\mathscr{Y}^*(a,\ell)} &= \|\psi\|_{L^{2,\infty}(I_a)} + \big\|\dot\psi\big\|_{\mathscr{X}^*(a,\ell)}.
\end{aligned}$$

See for further results on these operators and Banach spaces [Yaj87].

Using Lemma 4.3, we then have the following inequalities:

$$\forall f \in L^2(\mathbb{R}^3): \qquad \|U_0(\cdot)f\|_{\mathscr{X}(a,\ell)} \lesssim_{\theta(\ell)} \|f\|_{L^2(\mathbb{R}^3)}, \tag{4.7}$$

$$\forall \psi \in \mathscr{X}^*(a,\ell): \qquad \|S\psi\|_{\mathscr{X}(a,\ell)} \lesssim_{\theta(\ell)} \|\psi\|_{\mathscr{X}^*(a,\ell)}, \tag{4.8}$$

$$\forall \psi \in \mathscr{Y}^*(a,\ell): \qquad \|S\psi\|_{\mathscr{Y}(a,\ell)} \lesssim (1+a)\|\psi\|_{\mathscr{Y}^*(a,\ell)}. \tag{4.9}$$

Here, $A \lesssim_\alpha B$ means that $A \leq C_\alpha B$ for some constant $0 < C_\alpha < \infty$ depending on $\alpha$; see also Section A.1.
For the multiplication with the potential $V(t,x)$, we need the following results. We define the Banach spaces

$$\mathscr{M} := L^{p,\alpha}(I_a) + L^{\infty,\beta}(I_a), \widetilde{\mathscr{M}} := L^{\widetilde{p},\infty}(I_a) + L^{\infty,\infty}(I_a),$$
$$\mathscr{N} := L^{p_1,\alpha_1}(I_a) + L^{\infty,\beta}(I_a),$$

for which we the following inequalities hold:

1. Under Assumption 4.4, we have, with $\gamma := \min\left\{1 - \frac{1}{\beta}, 1 - \frac{3}{2p} - \frac{1}{\alpha}\right\}$,

$$\|V\psi\|_{\mathscr{X}^*(a,q)} \leq (2a)^\gamma \|V\|_{\mathscr{M}} \|\psi\|_{\mathscr{X}(a,q)} \tag{4.10}$$

   for $a < 1/2$,

2. Under Assumption 4.7, we have that

   - $\mathcal{V}$ maps $\mathscr{Y}(a,q^*)$ into $\mathscr{Y}^*(a,q^*)$ continuously, and
   - for all $\varepsilon > 0$, there is a constant $C_\varepsilon > 0$ such that for all $a < 1/2$

$$\begin{aligned}\|V\psi\|_{\mathscr{Y}^*(a,q^*)} \leq \left[\varepsilon\|V\|_{\widetilde{\mathscr{M}}} + (2a)^\kappa \left\|\dot{V}\right\|_{\mathscr{N}}\right] \|\psi\|_{\mathscr{Y}(a,q^*)} \\ + C_\varepsilon \|V\|_{\widetilde{\mathscr{M}}} \|\psi\|_{L^{2,\infty}(I_a)}\end{aligned}$$

   for all $\psi \in \mathscr{Y}(a,q^*)$. Here, $\kappa = \min\left\{\frac{1}{\theta(\ell)'} - \frac{1}{\alpha}, \gamma\right\}$.

We will later adapt the above results to our setting.

## 4.2 A brief literature review on similar coupled evolution problems

There exists an extensive body of literature on the mathematical and physical aspects of the type of models and systems we are studying, both in a time-dependent and a time-independent setting. The reader is referred to [Lie83; PZ81; PK03; BL05; Ull12] and the references therein, for various perspectives on models describing the dynamics of diverse molecular systems and the accompanying systems of (evolution) equations. In particular, given the difficulties the exchange-correlation potential poses, we highlight the articles [Jer15; AC09] and the references therein for a

treatment of a non-zero correlation potential in both a time-independent and a (specific) time-dependent settings.

In this section, we will shortly review contributions of other authors which we believe are the closest to our work.

Cancès & Le Bris [CB99] prove global-in-time existence and uniqueness of solutions

$$\psi^{\mathrm{HF}} \in C^0\big([0,+\infty); H^2\big(\mathbb{R}^3;\mathbb{C}^{N_{\mathrm{el}}}\big)\big) \cap C^1\big([0,+\infty); L^2\big(\mathbb{R}^3;\mathbb{C}^{N_{\mathrm{el}}}\big)\big),$$
$$X \in C^2\big([0,+\infty);\mathbb{R}^{3N_{\mathrm{nuc}}}\big)$$

to a model which couples similar electronic evolution equations (viz. the time-dependent Hartree–Fock equations) with classical nuclear dynamics for the nuclei, consistent with the mean-field Ehrenfest approach. This system is given by

$$i\dot{\psi}^{\mathrm{HF}} = H^{\mathrm{HF}}[X,\psi^{\mathrm{HF}}]\psi^{\mathrm{HF}}, \tag{4.11a}$$
$$\ddot{X} = A[\rho](X), \tag{4.11b}$$
$$\psi^{\mathrm{HF}}(0) = \psi^{\mathrm{HF},0}, \quad X(0) = X^{\mathrm{HF},0}, \quad \dot{X}(0) = V^{\mathrm{HF},0}, \tag{4.11c}$$

where $\rho^{\mathrm{HF}} = \sum_{k=1}^{N_{\mathrm{el}}} |\psi_k^{\mathrm{HF}}|^2$. Furthermore, the Hartree–Fock Hamiltonian is given by

$$H^{\mathrm{HF}}[X,\psi^{\mathrm{HF}}] = -\tfrac{1}{2}\Delta_x + \mathcal{V}_{\mathrm{ext}}[X] + \mathcal{V}_{\mathrm{H}}[\rho^{\mathrm{HF}}] + \mathcal{V}_{\mathrm{x}}^{\mathrm{HF}}[\psi^{\mathrm{HF}}], \tag{4.12}$$

where

$$(\mathcal{V}_{\mathrm{x}}^{\mathrm{HF}}[\psi^{\mathrm{HF}}]\psi^{\mathrm{HF}})_k = -\sum_{\ell=1}^{N_{\mathrm{el}}} \big(|\cdot|^{-1} * \overline{\psi_\ell^{\mathrm{HF}}}\psi_k^{\mathrm{HF}}\big)\psi_k^{\mathrm{HF}}, \tag{4.13}$$

is the *Hartree–Fock exchange potential*. Here, $\psi_k^{\mathrm{HF}}, k = 1,\dots,N_{\mathrm{el}}$, are single-particle wave functions as well.

In the article, the result of global-in-time existence and uniqueness of solutions of (4.11) in the setting of $H^2$ for $\psi^{\mathrm{HF}}$ is based on the celebrated result by Yajima (see [Yaj87] and Section 4.1) on the existence of propagators associated with the linear part of the time-dependent Hamiltonian $H^{\mathrm{HF}}$, which is the same as the linear part of our time-dependent Hamiltonian $H^{\mathrm{KS}}$. The result is the following Lemma, which is formulated only for the case $N_{\mathrm{el}} = N_{\mathrm{nuc}} = 1$ [CB99, Lemma 4]:

**Lemma 4.9** (Cancès & Le Bris)**.** *Let $\Theta > 0$ be the endpoint of a time interval $[0,\Theta]$. Furthermore, let $X \in C^1([0,\Theta];\mathbb{R}^3)$ and the family of Hamiltonians $\left\{H^{\mathrm{HF,lin}}(t), t \in [0,\Theta]\right\}$ be defined as*

$$H^{\mathrm{HF,lin}}(t) := -\tfrac{1}{2}\Delta_x + \mathcal{V}_{\mathrm{ext}}[X(t)].$$

*There exists a unique family of evolution operators*

$$\{U(t,s), t, s \in [0,\Theta]\}, \tag{4.14}$$

*such that*

1. *$U(t,s)U(s,r) = U(t,r)$ for all $t,s,r \in [0,\Theta]$.*
2. *$U(t,s)$ is a unitary operator on $L^2$ for all $t,s \in [0,\Theta]$:*

$$\|U(t,s)\psi\|_{L^2} = \|\psi\|_{L^2}. \tag{4.15}$$

3. *For all $f \in L^2$, $((t,s) \longmapsto U(t,s)f) : [0,\Theta]^2 \longrightarrow L^2$ is a continuous mapping.*
4. *$U(t,s) \in \mathcal{L}\big(H^2\big)$ for all $(t,s) \in [0,\Theta]^2$.*
5. *For all $f \in H^2$, $((t,s) \longmapsto U(t,s)f) : [0,\Theta]^2 \longrightarrow H^2$ is a continuous mapping.*
6. *For all $f \in H^2$, the mapping $((t,s) \longmapsto U(t,s)f) \in C^1\big([0,\Theta]^2; L^2\big)$, and the following equations hold in $L^2$:*

$$i\frac{\partial}{\partial t}(U(t,s)f) = H^{HF,lin}(t)U(t,s)f, \tag{4.16}$$

$$i\frac{\partial}{\partial s}(U(t,s)f) = -U(t,s)H^{HF,lin}(s)f. \tag{4.17}$$

7. *For all $\gamma > 0$, there is a constant $B_{\Theta,\gamma}$ of the form*

$$B_{\Theta,\gamma} = A_\gamma^{1+C_\gamma\Theta}, \qquad A_\gamma, C_\gamma > 1, \tag{4.18}$$

*such that if*

$$\left\|\dot{X}\right\|_{C^0([0,\Theta])} \leq \gamma, \tag{4.19}$$

*we have for all $t,s \in [0,\Theta]$*

$$\|U(t,s)\|_{\mathcal{L}(H^2)} \leq B_{\Theta,\gamma}. \tag{4.20}$$

*Proof.* The proof is given in detail in [CB99], where for the most properties, as the properties defining a strongly continuous semigroup, it is referred to [Yaj87]. Since we extend this result later in Section 4.3, we list the ideas that we will employ later on as well.

First, $X$ is extended to a $C^1$ function on $I_\Theta$, such that $\|\dot{X}\|_{L^\infty(I_\Theta)} = \|\dot{X}\|_{L^\infty(0,\Theta)}$. Furthermore, it is noted that $V(t,x) = V_{\mathrm{ext}}[X(t)](x)$ satisfies Assumption 4.7 for $\widetilde{p} \in [2,3)$ and $\alpha_1 = \beta = \infty$. Now, following the proof of Theorem 4.8, we obtain (as $N_{\mathrm{el}} = N_{\mathrm{nuc}} = 1$) by translation invariance and the chain rule

$$\|V\|_{\mathscr{M}} = \big\||Z|\cdot|^{-1}\big\|_{L^p+L^\infty}, \qquad \|\partial_t V\|_{\mathscr{N}} \le \|\dot{X}\|_{L^\infty(I_a)} \big\||Z|\cdot|^{-2}\big\|_{L^{p_1}+L^\infty}.$$

Now, since $\|\dot{X}\|_{L^\infty(I_a)} \le \|\dot{X}\|_{L^\infty(I_\Theta)} \le \gamma$, one can find for $\varepsilon > 0$ small enough a constant $0 < b_\gamma < 1/2$ such that there exists a constant $C_\gamma$ (both independent of $\psi^{\mathrm{HF},0}$) satisfying

$$\|\psi^{\mathrm{HF}}\|_{L^\infty((0,b_\gamma);H^2(\mathbb{R}^3))} \le \|\psi^{\mathrm{HF}}\|_{\mathscr{Y}(b_\gamma,q^*)} \le C_\gamma \|\psi^{\mathrm{HF},0}\|_{H^2(\mathbb{R}^3)}.$$

As a consequence, for $t \in [0,b_\gamma]$, $\|U(t,0)\|_{\mathcal{L}(H^2(\mathbb{R}^3))} \le C_\gamma$, and therefore by property (1) from the Lemma statement

$$\|U(t,0)\|_{\mathcal{L}(H^2(\mathbb{R}^3))} \le C_\gamma^{1+\Theta/b_\gamma} =: B_{\Theta,\gamma} \qquad \text{for all } t \in [0,\Theta].$$

The same result follows for $U(t,s), t, s \in [0,\Theta]$. □

We will revisit this Lemma later in order to really adapt it to our setting, in Lemma 4.12.

The remainder of the proof of global-in-time existence and uniqueness of solutions in [CB99] consists of two main steps: a Schauder fixed-point argument to show existence of short-time solutions, based on Lipschitz estimates of the non-linear part of $H^{\mathrm{HF}}\psi^{\mathrm{HF}}$ in $H^2$, and a Grönwall-type argument which relies on conservation in time of the total energy and electron charge, and estimates of the solutions $\psi^{\mathrm{HF}}$ in the $H^2$ norm.

Since the paper by Cancès & Le Bris [CB99] we discussed above, only a handful of contributions deal with a similar coupling of a system describing electronic evolution with nuclear dynamics: this is the case, for instance, for [Bau05]. Here, for a Hartree–Fock equation coupled with Newtonian nuclear dynamics, existence and regularity questions

in different function spaces have been studied. Other researchers have also studied Schrödinger–Poisson type equations, which include the Hartree–Fock and the time-dependent Kohn–Sham equations: see for instance [Mau01; Cat+13; BLS03; Zag92; CG75; Cas97; AC09; Jer15; BDF76; BDF74]. We also mention [SCB19], where existence, uniqueness, and regularity questions are investigated for time-dependent Kohn–Sham equations set on bounded space domains, in relation to control problems. However, none of the contributions listed above have considered the combined nuclear and electronic dynamics as described in our system combined.

## 4.3 Preliminary results

The first observation in this section is that the Newton potential

$$G[\phi_1, \phi_2] := \left(\overline{\phi_1}\, \phi_2\right) * |\cdot|^{-1}, \tag{4.21}$$

solution to $-\Delta_x G = 4\pi\overline{\phi_1}\phi_2$, defines a mapping: $H^2 \times H^2 \longrightarrow W^{2,\infty}$.

**Lemma 4.10.** *For all $i, k \in \{1, 2, 3\}$ and every $x \in \mathbb{R}^3$ it holds that*

$$|G[\phi_1, \phi_2](x)| \lesssim \|\phi_1\|_{L^2} \|\nabla_x \phi_2\|_{L^2}, \tag{4.22}$$

$$|\partial_i G[\phi_1, \phi_2](x)| \lesssim \|\nabla_x \phi_1\|_{L^2} \|\nabla_x \phi_2\|_{L^2}, \tag{4.23}$$

$$|\partial_{ij} G[\phi_1, \phi_2](x)| \lesssim \|\phi_1\|_{H^2} \|\phi_2\|_{H^2}. \tag{4.24}$$

Here, $A \lesssim B$ means that $A \leq CB$ for some constant $0 < C < \infty$; see also Section A.1.

*Proof.* Using Hardy's inequality (A.4) and the properties

$$\begin{aligned}
\partial_i G[\phi_1, \phi_2] &= \left(\overline{\phi_1}\phi_2\right) * \left(x_i |x|^{-3}\right), \\
\partial_{ij} G[\phi_1, \phi_2] &= \left[\left(\partial_i \overline{\phi_1}\right)\phi_2 + \overline{\phi_1}(\partial_j \phi_2)\right] * \left(x_i |x|^{-3}\right),
\end{aligned}$$

for all $i, j$ and $x \in \mathbb{R}^3$, we derive

$$\begin{aligned}
&|G[\phi_1, \phi_2](x)| = \left|\left(\phi_1, |\cdot - x|^{-1}\phi_2\right)_{L^2}\right| \lesssim \|\phi_1\|_{L^2} \|\nabla_x \phi_2\|_{L^2}, \\
&|\partial_i G[\phi_1, \phi_2](x)| \leq \left(|\cdot - x|^{-1}|\phi_1|, |\cdot - x|^{-1}|\phi_2|\right)_{L^2} \lesssim \|\nabla_x \phi_1\|_{L^2} \|\nabla_x \phi_2\|_{L^2}, \\
&|\partial_{ij} G[\phi_1, \phi_2](x)| \leq \left(|\cdot - x|^{-1}|\partial_i \phi_1|, |\cdot - x|^{-1}|\phi_2|\right)_{L^2} \\
&\qquad + \left(|\cdot - x|^{-1}|\phi_1|, |\cdot - x|^{-1}|\partial_j \phi_2|\right)_{L^2} \\
&\lesssim \|\nabla_x \partial_i \phi_1\|_{L^2} \|\nabla_x \phi_2\|_{L^2} + \|\nabla_x \phi_1\|_{L^2} \|\nabla_x \partial_j \phi_2\|_{L^2} \lesssim \|\phi_1\|_{H^2} \|\phi_2\|_{H^2}.
\end{aligned}$$

This concludes the proof. □

We now generalise [CB99, Lemma 3], on bounds for the following functions.

We define $f_K^{k\ell} : \mathbb{R}^{3N_{\mathrm{nuc}}} \longrightarrow \mathbb{C}^3$ (a.e.) as

$$f_K^{k\ell} := \nabla_{X_K}(\psi_k, V_{\mathrm{ext}}[X]\psi_\ell)_{L^2}, \tag{4.25}$$

namely,

$$f_K^{k\ell}(X) = -Z_K\Big(\psi_k, \frac{\cdot - X_K}{|\cdot - X_K|^3}\psi_\ell\Big)_{L^2}. \tag{4.26}$$

Note that $f_K^{k\ell}$ effectively only depends on $X_K$. Also,

$$A_K^1 = -\frac{1}{M_K}\sum_{k=1}^{N_{\mathrm{el}}} f_K^{kk}. \tag{4.27}$$

**Lemma 4.11.** *For all functions $\psi_k, \psi_\ell \in H^2$, the following estimates hold. For all $\psi_k, \psi_\ell \in H^1$,*

$$\big\|f_K^{k\ell}\big\|_{L^\infty(\mathbb{R}^{3N_{\mathrm{nuc}}};\mathbb{C}^3)} \lesssim \|\nabla_x\psi_k\|_{L^2}\|\nabla_x\psi_\ell\|_{L^2}, \tag{4.28}$$

*and for all $\psi_k, \psi_\ell \in H^2$,*

$$\big\|Df_K^{k\ell}\big\|_{L^\infty(\mathbb{R}^{3N_{\mathrm{nuc}}};\mathbb{C}^{3\times 3})} \lesssim \|\psi_k\|_{H^2}\|\psi_\ell\|_{H^2}. \tag{4.29}$$

*Here, $D$ is the gradient in $\mathbb{R}^{3N_{\mathrm{nuc}}}$. In addition, we have that $f_K^{k\ell} \in W^{1,\infty} \cap C^1$ for all $K$.*

*Proof.* By Lemma 4.10, $G[\phi_1, \phi_2] \in W^{2,\infty}$ for all $\phi_1, \phi_2 \in H^2$. Using

$$f_K^{k\ell}(X) = -Z_K\nabla_x G[\psi_k, \psi_\ell](X_K), \tag{4.30}$$

we get

$$\big\|f_K^{k\ell}\big\|_{L^\infty(\mathbb{R}^{3N_{\mathrm{nuc}}};\mathbb{C}^3)} \lesssim \|\nabla_x\psi_k\|_{L^2}\|\nabla_x\psi_\ell\|_{L^2}, \tag{4.31}$$

$$\begin{aligned}\big\|Df_K^{k\ell}\big\|_{L^\infty(\mathbb{R}^{3N_{\mathrm{nuc}}};\mathbb{C}^{3\times 3})} &\lesssim \max_{X_K\in\mathbb{R}^3}\big\|D^2G[\psi_k, \psi_\ell](X_K)\big\|_{\mathbb{C}^{3\times 3}} \\ &\lesssim \|\psi_k\|_{H^2}\|\psi_\ell\|_{H^2}.\end{aligned} \tag{4.32}$$

This shows that $f_K^{k\ell} \in W^{1,\infty}$. By Sobolev embedding in Hölder spaces, $\overline{\psi_k}\psi_\ell \in C^{0,\alpha}_{\mathrm{loc}}$. Using (4.21) from Lemma 4.10 and standard elliptic regularity, it holds that $G[\psi_k, \psi_\ell] \in C^2$, by which $f_K^{k\ell} \in C^1$. □

Now, the following results we derived for the existence of the propagator for the linear parts of the Kohn–Sham-type Hamiltonians $H^{\mathrm{KS}}[X(t), \rho]$ for $t \in [0, \Theta]$, with $0 < \Theta < \infty$, for a given nuclear configuration $X \in C^1([0, \Theta])$.

For given $X \in C^1\big([0, \Theta]; \mathbb{R}^{3N_{\mathrm{nuc}}}\big)$, for some $0 < \Theta < \infty$, we consider the family of linear time-dependent Hamiltonians $\{H^{\mathrm{KS,lin}}(t), t \in [0, \Theta]\} \subset \mathcal{L}\big(H^2\big(\mathbb{R}^3; \mathbb{C}^{N_{\mathrm{el}}}\big); L^2\big(\mathbb{R}^3; \mathbb{C}^{N_{\mathrm{el}}}\big)\big)$, with

$$H^{\mathrm{KS,lin}}(t) := -\tfrac{1}{2}\Delta_x + V(t), \tag{4.33}$$

with $V(t, \cdot) := V_{\mathrm{ext}}[X(t)]$. Note that the Hamiltonians $H^{\mathrm{KS,lin}}(t)$ correspond to the linear part of $H^{\mathrm{KS}}[X(t), \rho]$, and that they are self-adjoint on $L^2\big(\mathbb{R}^3; \mathbb{C}^{N_{\mathrm{el}}}\big)$. We also note that they depend on the time evolution of the nuclear configuration $X$. Associated with this family of Hamiltonians are the corresponding Cauchy problems

$$i\dot{\psi} = H^{\mathrm{KS,lin}}(t)\psi, \qquad \psi(s) = \psi^0, \tag{4.34}$$

on the time interval $[0, \Theta]$, for some $s \in [0, \Theta]$. For $s = 0$, this can be considered the linear part of the Cauchy problem associated to (4.1a) with $\psi(0) = \psi^0$. We also consider the equivalent integral equation

$$\psi(t) = U_0(t - s)\psi^0 - i \int_s^t U_0(t - \sigma)V(\sigma)\psi(\sigma)\mathrm{d}\sigma. \tag{4.35}$$

Now, we formulate the following Lemma in the spirit of [CB99, Lemma 4], based on the idea of [Yaj87, Cor. 1.2. (1)–(2)–(4), Thm. 1.1. (2) & Thm. 1.3. (5)–(6)].

**Lemma 4.12.** *For the family of Hamiltonians* $\big\{H^{\mathrm{KS,lin}}(t), t \in [0, \Theta]\big\}$, *there exists a unique family of linear evolution operators*

$$U(t, s) : L^2\big(\mathbb{R}^3; \mathbb{C}^{N_{\mathrm{el}}}\big) \longrightarrow L^2\big(\mathbb{R}^3; \mathbb{C}^{N_{\mathrm{el}}}\big), \qquad t, s \in [0, \Theta], \tag{4.36}$$

*such that*

$$\psi(t) := U(t, s)\psi^0 \tag{4.37}$$

*solves* (4.35) *on* $[0, \Theta]$ *for all* $\psi^0 \in H^2$, *with*

$$\|\psi(t)\|_{L^2} = \big\|\psi^0\big\|_{L^2} \tag{4.38}$$

*for all* $t \in [0, \Theta]$. *Moreover, this family enjoys the following properties:*

1. $U(t,s)U(s,r) = U(t,r)$ *for all* $t,s,r \in [0,\Theta]$.
2. $U(t,t) = \mathrm{Id}$ *for all* $t \in [0,\Theta]$.
3. $U(t,s)$ *is a unitary operator on* $L^2$ *for all* $t,s \in [0,\Theta]$*:*
$$\|U(t,s)\psi\|_{L^2} = \|\psi\|_{L^2}. \tag{4.39}$$
4. *For all* $\phi \in L^2$, $((t,s) \longmapsto U(t,s)\phi) : [0,\Theta]^2 \longrightarrow L^2$ *is a continuous mapping.*
5. $U(t,s) \in \mathcal{L}\big(H^2\big)$ *for all* $(t,s) \in [0,\Theta]^2$.
6. *For all* $\phi \in H^2$, $((t,s) \longmapsto U(t,s)\phi) : [0,\Theta]^2 \longrightarrow H^2$ *is a continuous mapping.*
7. *For all* $\phi \in H^2$, *the mapping* $(t,s) \longmapsto U(t,s)\phi$ *is an element in* $C^1\big([0,\Theta]^2; L^2\big)$, *and the following equations hold in* $L^2$*:*
$$i\frac{\partial}{\partial t}(U(t,s)\phi) = H^{\mathrm{KS,lin}}(t)U(t,s)\phi, \tag{4.40}$$
$$i\frac{\partial}{\partial s}(U(t,s)\phi) = -U(t,s)H^{\mathrm{KS,lin}}(s)\phi. \tag{4.41}$$
8. *For all* $\gamma > 0$, *there is a constant* $B_{\Theta,\gamma}$ *of the form*
$$B_{\Theta,\gamma} = A_\gamma^{1+C_\gamma\Theta}, \qquad A_\gamma, C_\gamma > 1, \tag{4.42}$$
*such that if*
$$\big\|\dot{X}\big\|_{C^0([0,\Theta])} \leq \gamma, \tag{4.43}$$
*we have for all* $t,s \in [0,\Theta]$
$$\|U(t,s)\|_{\mathcal{L}\left(H^2\right)} \leq B_{\Theta,\gamma}. \tag{4.44}$$

*Proof.* The proof is an adaptation of the proofs of Theorem 4.8 and Lemma 4.9. In that regard, the proof is given in detail in [CB99], where for the most properties, as the properties defining a strongly continuous semigroup, it is referred to [Yaj87].
Since the linear Hamiltonians $H^{\mathrm{KS,lin}}(t)$ do not depend on an electronic

configuration $\psi$, and act on every element $\psi_k$ independently, the result for general $N_{\mathrm{el}}$ readily follows from the case $N_{\mathrm{el}} = 1$. Properties (1)–(7) have been proven for the case $N_{\mathrm{el}} = 1$ in [Yaj87, Cor. 1.2. (1)–(2)–(4), Thm. 1.1. (2) & Thm. 1.3. (5)–(6)]: see the proof of Theorem 4.8. Property (viii) has been proven for the case $N_{\mathrm{el}} = N_{\mathrm{nuc}} = 1$ in [CB99, Lemma 4], which on its own follows the results in [Yaj87]: see the proof of Lemma 4.9. We therefore justify (viii) for the case $N_{\mathrm{el}} = 1, N_{\mathrm{nuc}} > 1$, which only needs some additional changes. For all $a \in [0, \Theta]$, we get, with $p \in [2, 3)$ and $p_1 = 2p(p+1)^{-1}$, the following norms for $V$ and its time derivative $\dot{V}$:

$$\|V\|_{\widetilde{\mathcal{M}}} = \inf_{\substack{V_1, V_2: \\ V = V_1 + V_2 \text{ a.e.}}} \Big\{ \|V_1\|_{L^\infty([-a,a];L^p)} + \|V_2\|_{L^\infty([-a,a];L^\infty)} \Big\}, \tag{4.45}$$

$$\big\|\dot{V}_{\mathrm{ext}}\big\|_{\mathcal{N}} = \inf_{\substack{W_1, W_2: \\ \dot{V} = W_1 + W_2 \text{ a.e.}}} \Big\{ \|W_1\|_{L^\infty([-a,a];L^{p_1})} + \|W_2\|_{L^\infty([-a,a];L^\infty)} \Big\}.$$

Note that (4.45) is a bounded quantity, independent of $X$. Using the chain rule,

$$\big\|\dot{V}\big\|_{\mathcal{N}} \leq \gamma \sup_{\substack{w_1, w_2: \\ \nabla_X V_{\mathrm{ext}}[X] = w_1 + w_2 \text{ a.e.}}} \big\{ \|w_1\|_{L^{p_1}} + \|w_2\|_{L^\infty} \big\}.$$

Now, we conclude the proof as carried out in the proof of Lemma 4.9. □

## 4.4 Definition of the feasible regions

Fix some arbitrary time $0 < T < \infty$, and let $\tau \leq T$. Set

$$\gamma := \big|V^0\big| + 1, \tag{4.46}$$

where the addition "+1" is needed to cover the case where $V^0 = 0$. Using this quantity $\gamma$ and setting $\Theta = \tau$ in Lemma 4.12, we construct the quantities $B_{\tau,\gamma}$. We define the radius

$$\alpha(\tau) := 2B_{\tau,\gamma}\big\|\psi^0\big\|_{H^2} \tag{4.47}$$

for the ball centred around the initial configuration $\psi^0 \in H^2$:

$$B_\alpha\big(\psi^0\big) = \big\{\psi \in H^2 \big| \big\|\psi - \psi^0\big\|_{H^2} \leq \alpha\big\}. \tag{4.48}$$

We define the *electronic feasible region* for the time interval $[0,\tau]$ as

$$\mathcal{B}_{\mathrm{el}}(\tau) := \big\{\psi \in C^1\big([0,\tau];L^2\big(\mathbb{R}^3;\mathbb{C}^{N_{\mathrm{el}}}\big)\big) \cap C^0\big([0,\tau];B_\alpha\big(\psi^0\big)\big) \\ \mid \psi(0)=\psi^0\big\}, \tag{4.49}$$

equipped with the $C^0\big([0,\tau];L^2\big)$ norm, which is designed to contain short-time solutions $\psi$ to (4.107) on the time interval $[0,\tau]$, which we call *feasible electronic configurations*.

For all $0<\varepsilon<\min_{K\neq L}\big|X_K^0-X_L^0\big|$, we set

$$\delta(\tau) := \frac{\min_{K\neq L}\big|X_K^0-X_L^0\big| - \min\{\delta_{\mathrm{rep}}(\tau),\varepsilon\}}{2} > 0, \tag{4.50}$$

where

$$\delta_{\mathrm{rep}}(\tau) := \Bigg[\bigg(\sum_{K=1}^{N_{\mathrm{nuc}}} M_K\big|V_K^0\big|^2 + \sum_{\substack{K,L=1,\\ L\neq K}}^{N_{\mathrm{nuc}}} \frac{Z_K Z_L}{\big|X_K^0-X_L^0\big|}\bigg)\mathrm{e}^{\tau} \\ + 16\sum_{K=1}^{N_{\mathrm{nuc}}}\frac{Z_K^2}{M_K}\|\psi\|^2_{C^0([0,\tau];H^1)}\big(\mathrm{e}^{\tau}-1\big)\Bigg]^{-1} \tag{4.51}$$

arises from a repulsion argument. Note that $\varepsilon>0$ ensures the strict positivity of $\delta(\tau)$, which defines the radius for the ball centred around the initial configuration $X^0\in\mathbb{R}^{3N_{\mathrm{nuc}}}$, with $X_K^0\neq X_L^0$ for $K\neq L$:

$$B_\delta(X^0) = \big\{X\in\mathbb{R}^{3N_{\mathrm{nuc}}}\big|\big|X-X^0\big|\leq\delta\big\}. \tag{4.52}$$

Then, by the triangle inequality, for all $X\in B_\delta\big(X^0\big)$ and $K\neq L$, it holds that

$$\begin{aligned}|X_K-X_L| &\geq \min_{K'\neq L'}\big|X_{K'}^0-X_{L'}^0\big| - 2\big|X-X^0\big| \\ &\geq \min_{K'\neq L'}\big|X_{K'}^0-X_{L'}^0\big| - 2\delta(\tau) = \min\{\delta_{\mathrm{rep}}(\tau),\varepsilon\} > 0.\end{aligned} \tag{4.53}$$

We define the nuclear feasible region for the time interval $[0,\tau]$ as

$$\mathcal{B}_{\mathrm{nuc}}(\tau) := \Big\{X\in C^1\big([0,\tau];B_\delta\big(X^0\big)\big)\ \Big|\ X(0)=X^0, \dot X(0)=V^0, \\ \big\|\dot X\big\|_{C^0\left([0,\tau];\mathbb{R}^{3N_{\mathrm{nuc}}}\right)}\leq\gamma\Big\} \tag{4.54}$$

with $\gamma$ as in (4.46). This region is equipped with the $C^0\big([0,\tau];\mathbb{R}^{3N_{\mathrm{nuc}}}\big)$ topology, and is designed to contain short-time solutions $X$ to the initial-value problem associated to (4.1b) on the interval $[0,\tau]$, which we call feasible nuclear configurations.

This definition of $\delta(\tau)$ is suggested by an a priori lower bound on the nuclear distances $|X_K(t) - X_L(t)|$, $K \neq L$, which is based on Grönwall's Lemma.

**Lemma 4.13.** *Fix $\psi \in C^0\big([0,\tau];H^1\big)$, and $X^0 \in \mathbb{R}^{3N_{\mathrm{nuc}}}$ such that $X^0_K \neq K_L$. Let $X$ solve (4.1b), and $X(0) = X^0$. Then, we get for all $t \in [0,\tau]$ and $K \neq L$*

$$|X_K(t) - X_L(t)| \geq \delta_{rep}(\tau). \tag{4.55}$$

*for the nuclear trajectories.*

*Proof.* Writing the momenta $P_K := M_K \dot{X}_K$, we define the classical reduced Hamiltonian

$$\mathcal{H}_{\mathrm{nn}}(X,P) := \tfrac{1}{2}\sum_{K=1}^{N_{\mathrm{nuc}}} \frac{|P_K|^2}{M_K} + W_{\mathrm{nn}}(X) \tag{4.56}$$

with $W_{\mathrm{nn}}$ as in (3.11): note that $\mathcal{H}_{\mathrm{nn}}$ consists of the terms in the total energy (3.14) which only contain nuclear (so, classical) contributions: the nuclear kinetic energy and the nuclear repulsion term.

Fix $\psi \in C^0\big([0,\tau];H^1\big)$. Now,

$$\begin{aligned}
\frac{\mathrm{d}}{\mathrm{d}t}[\mathcal{H}_{\mathrm{nn}}(X,P)] &= \sum_{K=1}^{N_{\mathrm{nuc}}} \big[\nabla_{X_K}\mathcal{H}_{\mathrm{nn}}(X,P)\cdot\dot{X}_K + \nabla_{P_K}\mathcal{H}_{\mathrm{nn}}(X,P)\cdot\dot{P}_K\big] \\
&= \sum_{K=1}^{N_{\mathrm{nuc}}} \frac{P_K}{M_K}\cdot\{\nabla_{X_K}[W_{\mathrm{nn}}(X)] + M_K\ddot{X}_K\} \\
&\overset{(4.1b)}{=} -\sum_{K=1}^{N_{\mathrm{nuc}}} \frac{P_K}{M_K}\cdot(\nabla_{X_K}V_{\mathrm{ext}}[X],\rho)_{L^2} && (4.57)\\
&\leq \sum_{K=1}^{N_{\mathrm{nuc}}} \frac{1}{2M_K}\big[|P_K|^2 + |(\nabla_{X_K}V_{\mathrm{ext}}[X],\rho)_{L^2}|^2\big] && (4.58)\\
&\leq \mathcal{H}_{\mathrm{nn}}(X,P) + 8\sum_{K=1}^{N_{\mathrm{nuc}}} \frac{Z_K^2}{M_K}\|\psi\|^2_{C^0([0,\tau];H^1)}, && (4.59)
\end{aligned}$$

by which, using Grönwall's inequality (A.15), on $[0,\tau]$

$$\begin{aligned}
&\mathcal{H}_{\mathrm{nn}}(X,P) \leq \\
&\leq \tfrac{1}{2}\mathrm{e}^{\tau}\Bigg[\sum_{K=1}^{N_{\mathrm{nuc}}} M_K\big|V_K^0\big|^2 + \sum_{\substack{K,L=1,\\ L\neq K}}^{N_{\mathrm{nuc}}} \frac{Z_K Z_L}{|X_K^0 - X_L^0|} + 16\sum_{K=1}^{N_{\mathrm{nuc}}} \frac{Z_K^2}{M_K}\|\psi\|^2_{C^0([0,\tau];H^1)}\Bigg] \\
&\quad - 8\sum_{K=1}^{N_{\mathrm{nuc}}} \frac{Z_K^2}{M_K}\|\psi\|^2_{C^0([0,\tau];H^1)}. \qquad (4.60)
\end{aligned}$$

In (4.57), we use that $(V_{\mathrm{ext}}[X],\rho)_{L^2}$ is bounded using the Cauchy–Schwarz inequality together with the fact that $V_{\mathrm{ext}}[X] \in L^2 + L^\infty$ for all $X \in \mathbb{R}^{3N_{\mathrm{nuc}}}$, and that $\rho \in L^1 \cap L^2$ since $\psi \in H^2$. In (4.58), we use Young's inequality for products (A.14), and in (4.59), we use that $W_{\mathrm{nn}} \geq 0$ and that for all $K = 1,\dots,N_{\mathrm{nuc}}$

$$\begin{aligned}
&|(\nabla_{X_K} V_{\mathrm{ext}}[X],\rho)_{L^2}| = \\
&= \Big|\Big(-Z_K\frac{x-X_K}{|x-X_K|^3},\rho\Big)_{L^2}\Big| \leq Z_K\sum_{k=1}^{N_{\mathrm{el}}}\big\||x-X_K|^{-1}\psi_k\big\|_{L^2} \qquad (4.61)\\
&\leq 2Z_K\sum_{k=1}^{N_{\mathrm{el}}}\|\nabla_x\psi_k\|_{L^2} \leq 2\sqrt{2}Z_K\|\nabla_x\psi\|_{L^2} \leq 2\sqrt{2}Z_K\|\psi\|_{H^1}
\end{aligned}$$

by Hardy's inequality (A.4). Using the Grönwall bound (4.60) for $\mathcal{H}_{\mathrm{nn}}$, we derive a lower bound for the inter-nuclear distances. As $\mathcal{H}_{\mathrm{nn}}$ only contains positive terms and $Z_K \in \mathbb{N}$ for all $K$, we have for all $K \neq L$

$$\tfrac{1}{2}\frac{1}{|X_K - X_L|} \leq \frac{1}{Z_K Z_L}W_{\mathrm{nn}}(X) \leq W_{\mathrm{nn}}(X) \leq \mathcal{H}_{\mathrm{nn}}(X,P).$$

Combining this with (4.60), the result follows. □

**Remark 4.14.** A similar argument yields an a priori estimate of the nuclear velocity $\dot{X}$.

## 4.5 Lipschitz estimates

In the following Lemmas, we obtain Lipschitz estimates on the mapping

$$\psi \longmapsto \mathcal{V}_{\mathrm{HX}}[\rho]\psi := (\mathcal{V}_{\mathrm{H}}[\rho] + \mathcal{V}_{\mathrm{x}}[\rho])\psi. \qquad (4.62)$$

**Lemma 4.15** (Lipschitz estimates on the Hartree term)**.** *For all $\psi, \psi' \in H^1$, with $\rho' := |\psi'|^2$, we have*

$$\|\mathcal{V}_{\mathrm{H}}[\rho]\psi - \mathcal{V}_{\mathrm{H}}[\rho']\psi'\|_{L^2} \lesssim \sqrt{N_{\mathrm{el}}}\|\psi - \psi'\|_{L^2} \times \left[\sum_{k=1}^{N_{\mathrm{el}}}(\|\nabla_x\psi_k\|_{L^2} + \|\nabla_x\psi'_k\|_{L^2})\|\psi'\|_{L^2} + \sum_{\ell=1}^{N_{\mathrm{el}}}\|\psi_\ell\|_{L^2}\|\nabla_x\psi_\ell\|_{L^2}\right]. \quad (4.63)$$

*Additionally, for all $\psi, \psi' \in H^2$ we have*

$$\|\mathcal{V}_{\mathrm{H}}[\rho]\psi\|_{H^2} \lesssim \sqrt{N_{\mathrm{el}}}\sum_{k=1}^{N_{\mathrm{el}}}\|\psi_k\|_{H^1}^2\|\psi\|_{H^2} \quad (4.64)$$

*and*

$$\|\mathcal{V}_{\mathrm{H}}[\rho]\psi - \mathcal{V}_{\mathrm{H}}[\rho']\psi'\|_{H^2} \lesssim \lesssim \sqrt{N_{\mathrm{el}}}\|\psi - \psi'\|_{H^2}\sum_{k=1}^{N_{\mathrm{el}}}\left[(\|\psi_k\|_{H^1} + \|\psi'_k\|_{H^1})\|\psi'\|_{H^2} + \|\psi_k\|_{H^1}^2\right]. \quad (4.65)$$

*Proof. Proof of* (4.63).
By adding and subtracting the term $\left(|\psi_\ell|^2 * |\cdot|^{-1}\right)\psi'_k$, for all $k = 1, \ldots, N_{\mathrm{el}}$

$$\|(\mathcal{V}_{\mathrm{H}}[\rho]\psi - \mathcal{V}_{\mathrm{H}}[\rho']\psi')_k\|_{L^2} \leq \leq \sum_{\ell=1}^{N_{\mathrm{el}}}\Big[\underbrace{\big\|\left(|\psi_\ell|^2 * |\cdot|^{-1}\right)(\psi_k - \psi'_k)\big\|_{L^2}}_{=:\,(\mathrm{I})} + \underbrace{\big\|\left((|\psi_\ell|^2 - |\psi'_\ell|^2) * |\cdot|^{-1}\right)\psi'_k\big\|_{L^2}}_{=:\,(\mathrm{II})}\Big].$$

Using the Cauchy–Schwarz inequality in (4.66,4.68), Hardy's inequality (A.4) in (4.67,4.69), and the reverse triangle inequality in (4.69), we have

$$\begin{aligned}(\mathrm{I}) &\leq \big\||\psi_\ell|^2 * |\cdot|^{-1}\big\|_{L^\infty}\|\psi_k - \psi'_k\|_{L^2} \\ &\leq \operatorname*{esssup}_{x\in\mathbb{R}^3}\big\{\big|\big(|\psi_\ell|, |\cdot - x|^{-1}|\psi_\ell|\big)_{L^2}\big|\big\}\|\psi - \psi'\|_{L^2} \\ &\leq \operatorname*{esssup}_{x\in\mathbb{R}^3}\big\{\|\psi_k\|_{L^2}\big\||\cdot - x|^{-1}\psi_\ell\big\|_{L^2}\big\}\|\psi - \psi'\|_{L^2} \quad (4.66)\\ &\lesssim \|\psi_\ell\|_{L^2}\|\nabla_x\psi_\ell\|_{L^2}\|\psi - \psi'\|_{L^2}, \quad (4.67)\end{aligned}$$

and

$$\begin{aligned}
(\mathrm{II}) &\le \big\| \big(|\psi_\ell|^2 - |\psi_\ell'|^2\big) * |\cdot|^{-1} \big\|_{L^\infty} \|\psi_k'\|_{L^2} \\
&\le \operatorname*{esssup}_{x\in\mathbb{R}^3} \big\{ \big| \big(|\psi_\ell| - |\psi_\ell'|, |\cdot - x|^{-1}(|\psi_\ell| + |\psi_\ell'|)\big)_{L^2} \big| \big\} \|\psi'\|_{L^2} \\
&\le \operatorname*{esssup}_{x\in\mathbb{R}^3} \big\{ \big\| |\psi_\ell| - |\psi_\ell'| \big\|_{L^2} \big( \big\| |\cdot - x|^{-1} \psi_\ell \big\|_{L^2} + \big\| |\cdot - x|^{-1} \psi_\ell' \big\|_{L^2} \big) \big\} \|\psi'\|_{L^2} \qquad (4.68) \\
&\lesssim (\|\nabla_x \psi_\ell\|_{L^2} + \|\nabla_x \psi_\ell'\|_{L^2}) \|\psi'\|_{L^2} \|\psi_\ell - \psi_\ell'\|_{L^2} \qquad (4.69) \\
&\lesssim (\|\nabla_x \psi_\ell\|_{L^2} + \|\nabla_x \psi_\ell'\|_{L^2}) \|\psi'\|_{L^2} \|\psi - \psi'\|_{L^2}.
\end{aligned}$$

By this, estimate (4.63) follows.

*Proof of* (4.64).
Adopting the map $G$ from (4.21), we have

$$\mathcal{V}_{\mathrm{H}}[\rho]\psi = \sum_{k=1}^{N_{\mathrm{el}}} G[\psi_k, \psi_k]\psi. \qquad (4.70)$$

We obtain for all $\phi_1, \phi_2, \phi_3 \in H^2$, using the product rule for the Laplacian,

$$\Delta_x (G[\phi_1, \phi_2]\phi_3) = G[\phi_1, \phi_2]\Delta_x \phi_3 + 2\nabla_x (G[\phi_1, \phi_2]) \cdot \nabla_x \phi_3 - 4\pi \overline{\phi_1} \phi_2 \phi_3.$$

We have the following estimates, using (4.22,4.23) from Lemma 4.10:

$$\begin{aligned}
&\|G[\phi_1, \phi_2]\phi_3\|_{L^2} \le \|G[\phi_1, \phi_2]\|_{L^\infty} \|\phi_3\|_{L^2} \lesssim \|\phi_1\|_{H^1} \|\phi_2\|_{H^1} \|\phi_3\|_{H^1}, \\
&\|G[\phi_1, \phi_2]\Delta_x \phi_3\|_{L^2} \le \|G[\phi_1, \phi_2]\|_{L^\infty} \|\Delta_x \phi_3\|_{L^2} \lesssim \|\phi_1\|_{H^1} \|\phi_2\|_{H^1} \|\phi_3\|_{H^2}, \\
&\|\nabla_x (G[\phi_1, \phi_2]) \cdot \nabla_x \phi_3\|_{L^2} \le \|G[\phi_1, \phi_2]\|_{W^{1,\infty}} \|\nabla_x \phi_3\|_{L^2} \\
&\qquad \lesssim \|\phi_1\|_{H^1} \|\phi_2\|_{H^1} \|\phi_3\|_{H^1}.
\end{aligned}$$

Furthermore, using Hölder's inequality (A.5) and the Sobolev embedding in Corollary A.10, we have

$$\big\| \overline{\phi_1} \phi_2 \phi_3 \big\|_{L^2} \le \|\phi_1\|_{L^6} \|\phi_2\|_{L^6} \|\phi_3\|_{L^6} \lesssim \|\phi_1\|_{H^1} \|\phi_2\|_{H^1} \|\phi_3\|_{H^1}.$$

This gives for all $k$

$$\|(\mathcal{V}_{\mathrm{H}}[\rho]\psi)_k\|_{H^2} \le \sum_{\ell=1}^{N_{\mathrm{el}}} \|G[\psi_\ell, \psi_\ell]\psi_k\|_{H^2} \lesssim \sum_{k=1}^{N_{\mathrm{el}}} \|\psi_k\|_{H^1}^2 \|\psi\|_{H^2}.$$

By this, (4.64) follows.

*Proof of* (4.65).
Following the first line in the Proof of (4.63), for all $k = 1, \dots, N_{\mathrm{el}}$

$$\|\Delta_x(\mathcal{V}_{\mathrm{H}}[\rho]\psi - \mathcal{V}_{\mathrm{H}}[\rho']\psi')_k\|_{L^2} \leq \sum_{\ell=1}^{N_{\mathrm{el}}} \Big\{ \underbrace{\|\Delta_x[G[\psi_\ell, \psi_\ell](\psi_k - \psi'_k)]\|_{L^2}}_{=:\,(\mathrm{I})} + \underbrace{\|\Delta_x[G[|\psi_\ell| + |\psi'_\ell|, |\psi_\ell| - |\psi'_\ell|]\psi'_k]\|_{L^2}}_{=:\,(\mathrm{II})} \Big\}.$$

Using the estimates in the Proof of (4.64), we bound (I) and (II) using $(\phi_1, \phi_2, \phi_3) = (\psi_\ell, \psi_\ell, \psi_k - \psi'_k)$ for (I) and $(\phi_1, \phi_2, \phi_3) = (|\psi_\ell| + |\psi'_\ell|, |\psi_\ell| - |\psi'_\ell|, \psi_k)$ for (II). This way, using the reverse triangle inequality $||\psi_\ell| - |\psi'_\ell|| \leq |\psi_\ell - \psi'_\ell|$,

$$\begin{aligned} &\|\Delta_x(\mathcal{V}_{\mathrm{H}}[\rho]\psi - \mathcal{V}_{\mathrm{H}}[\rho']\psi')\|_{L^2} \lesssim (\mathrm{B}) := \\ &= \sqrt{N_{\mathrm{el}}} \sum_{k=1}^{N_{\mathrm{el}}} \big[\|\psi_k\|_{H^1}^2 + (\|\psi_k\|_{H^1} + \|\psi'_k\|_{H^1})\|\psi'\|_{H^2}\big]\|\psi - \psi'\|_{H^2}. \end{aligned} \tag{4.71}$$

Via estimate (4.63), we also bound

$$\|\mathcal{V}_{\mathrm{H}}[\rho]\psi - \mathcal{V}_{\mathrm{H}}[\rho']\psi'\|_{L^2} \lesssim (\mathrm{B}). \tag{4.72}$$

Combining (4.71,4.72) with the norm on $H^2$ (see also A.2), (4.65) directly follows. □

Using the Cartesian norm for the tensor $\nabla_x\psi$, with $\psi$ a $\mathbb{C}^{N_{\mathrm{el}}}$-valued function, and the Cauchy–Schwarz inequality, we obtain the following inequality for $\mathbb{C}^{N_{\mathrm{el}}}$-valued functions $\psi, \psi'$:

$$|\psi \cdot \nabla_x\psi'| \leq |\psi||\nabla_x\psi'|. \tag{4.73}$$

**Lemma 4.16** (Mean-value estimates for the density)**.** *For $a \geq 1/2$, we have*

$$\big|\rho^a - \rho'^a\big| \lesssim_a \big(\|\rho\|_{L^\infty}^{a-1/2} + \|\rho'\|_{L^\infty}^{a-1/2}\big)|\psi - \psi'|. \tag{4.74}$$

*Proof.* We have, by the fundamental theorem of calculus,

$$\begin{aligned}
&\big|\rho^a - \rho'^a\big| = \big||\psi|^{2a} - |\psi'|^{2a}\big| = \Big|\int_0^1 \frac{\mathrm{d}}{\mathrm{d}t}\big[|\psi' + t(\psi - \psi')|^{2a}\big]\mathrm{d}t\Big| \\
&\lesssim_a (|\psi| + |\psi'|)^{2a-1}|\psi - \psi'| \lesssim_a \big(|\psi|^{2a-1} + |\psi'|^{2a-1}\big)|\psi - \psi'| \\
&= \big(\rho^{a-1/2} + \rho'^{a-1/2}\big)|\psi - \psi'|,
\end{aligned}$$

and (4.74) readily follows. □

**Lemma 4.17** (Mean-value estimates for the density gradient)**.** *For $b \geq 3/2$, we have*

$$\begin{aligned}
&\big|\nabla_x\big(\rho^b\big) - \nabla_x\big(\rho'^b\big)\big| \lesssim_b \\
&\lesssim_b (Q_1|\nabla_x\psi| + Q_2|\nabla_x\psi'|)|\psi - \psi'| + Q_3|\nabla_x\psi - \nabla_x\psi'|,
\end{aligned} \tag{4.75}$$

*where*

$$Q_1 = \rho^{b-1}, \quad Q_2 = \rho'^{1/2}\big(\rho^{b-3/2} + \rho'^{b-3/2}\big), \quad Q_3 = \rho^{b-1}\rho'^{1/2}.$$

*Proof.* We have, using $\nabla_x\rho = \nabla_x\psi \cdot \overline{\psi} + \psi \cdot \nabla_x\big(\overline{\psi}\big)$ and (4.73) for the pair $(\psi, \overline{\psi})$,

$$|\nabla_x\rho| \lesssim \rho^{1/2}|\nabla_x\psi|. \tag{4.76}$$

Using

$$\big|\nabla_x\big(\rho^b\big)\big| \lesssim_b \rho^{b-1}|\nabla_x\rho|$$

and adding and subtracting the term $\rho^{b-1}\nabla_x\rho'$, we get for all $b \geq 1$

$$\big|\nabla_x\big(\rho^b\big) - \nabla_x\big(\rho'^b\big)\big| \lesssim_b \rho^{b-1}|\nabla_x\rho - \nabla_x\rho'| + \big|\rho^{b-1} - \rho'^{b-1}\big||\nabla_x\rho'|.$$

By adding and subtracting $\psi' \cdot \nabla_x\big(\overline{\psi}\big)$ and $\overline{\psi'} \cdot \nabla_x\psi$, and using (4.73) for the pairs $\big(\psi - \psi', \overline{\psi}\big)$, $\big(\psi', \overline{\psi - \psi'}\big)$, $\big(\overline{\psi - \psi'}, \psi\big)$ and $\big(\overline{\psi'}, \psi - \psi'\big)$, we get

$$\begin{aligned}
&|\nabla_x\rho - \nabla_x\rho'| = \\
&= \big|\psi \cdot \nabla_x\big(\overline{\psi}\big) - \psi' \cdot \nabla_x\big(\overline{\psi'}\big) + \overline{\psi} \cdot \nabla_x\psi - \overline{\psi'} \cdot \nabla_x(\psi')\big| \\
&\leq \big|(\psi - \psi') \cdot \nabla_x\big(\overline{\psi}\big)\big| + \big|\psi' \cdot \nabla_x\big(\overline{\psi - \psi'}\big)\big| + \big|\big(\overline{\psi - \psi'}\big) \cdot \nabla_x(\psi)\big| \\
&\qquad + \big|\overline{\psi'} \cdot \nabla_x(\psi - \psi')\big| \\
&\lesssim |\nabla_x\psi||\psi - \psi'| + \rho'^{1/2}|\nabla_x\psi - \nabla_x\psi'|.
\end{aligned} \tag{4.77}$$

Using (4.74) with $a = b - 1 \geq 1/2$ and (4.76) for $\rho'$, we get

$$\big|\rho^{b-1} - \rho'^{b-1}\big||\nabla_x\rho'| \lesssim_b \big(\rho^{b-3/2} + \rho'^{b-3/2}\big)\rho'^{1/2}|\nabla_x\psi'||\psi - \psi'|.$$

These estimates altogether give the result in (4.75). □

**Lemma 4.18** (Lipschitz estimates on the local nonlinearity)**.** *Let $q \in [1,\infty)$, and $\lambda \in \mathbb{R}$. For any fixed $p \in [1,\infty]$ and for all $\psi, \psi' \in H^2 \cap L^p$, we have*

$$\|\mathcal{V}_{\mathrm{x}}[\rho]\psi - \mathcal{V}_{\mathrm{x}}[\rho']\psi'\|_{L^p} \lesssim_{q,\lambda} \sum_{k=1}^{N_{\mathrm{el}}} \Big[\|\psi_k\|_{H^2}^{2(q-1)} + \|\psi_k'\|_{H^2}^{2(q-1)}\Big] \|\psi - \psi'\|_{L^p}. \tag{4.78}$$

*Moreover, for all $q \geq 7/2$ and any $\lambda \in \mathbb{R}$, it holds that*

$$\|\mathcal{V}_{\mathrm{x}}[\rho]\psi - \mathcal{V}_{\mathrm{x}}[\rho']\psi'\|_{H^2} \leq \mathcal{L}_{q,\lambda}(\max\{\|\psi\|_{H^2}, \|\psi'\|_{H^2}\})\|\psi - \psi'\|_{H^2}, \tag{4.79}$$

*where $\mathcal{L}_{q,\lambda} : \mathbb{R}_0^+ \longrightarrow \mathbb{R}_0^+$ is a strictly increasing function near the origin.*

*Proof. Proof of* (4.78).
By the fundamental theorem of calculus,

$$\begin{aligned}
&|\mathcal{V}_{\mathrm{x}}[\rho]\psi - \mathcal{V}_{\mathrm{x}}[\rho']\psi'| = |\lambda|\big||\psi|^{2(q-1)}\psi - |\psi'|^{2(q-1)}\psi'\big| \\
&\lesssim_\lambda \Big| \int_0^1 \frac{\mathrm{d}}{\mathrm{d}t}\Big[|\psi' + t(\psi - \psi')|^{2(q-1)}(\psi' + t(\psi - \psi'))\Big]\mathrm{d}t\Big| \\
&\lesssim_q |\psi - \psi'| \int_0^1 |\psi' + t(\psi - \psi')|^{2(q-1)}\mathrm{d}t \leq |\psi - \psi'|\big(|\psi'| + |\psi|\big)^{2(q-1)} \\
&\lesssim_q \big(\rho^{q-1} + \rho'^{q-1}\big)|\psi - \psi'|.
\end{aligned}$$

Since $H^2$ is embedded into $L^\infty$, we have

$$\|\rho\|_{L^\infty}^a \lesssim_a \sum_{k=1}^{N_{\mathrm{el}}} \|\psi_k\|_{H^2}^{2a}, \tag{4.80}$$

for all $a > 0$. Taking $a = q - 1 > 0$ and combining the results, (4.78) follows.

*Proof of* (4.79).
Taking $p = 2$ in (4.78), we only need the $L^2$ norm of $\Delta_x(\mathcal{V}_{\mathrm{x}}[\rho]\psi - \mathcal{V}_{\mathrm{x}}[\rho']\psi')$ in addition to get the $H^2$ norm estimate. Using the product rule for the Laplacian in $\mathbb{R}^3$, we get

$$\begin{aligned}
\Delta_x(\mathcal{V}_{\mathrm{x}}[\rho]\psi - \mathcal{V}_{\mathrm{x}}[\rho']\psi') = \lambda\Big\{ &\underbrace{\rho^{q-1}\Delta_x\psi - \rho'^{q-1}\Delta_x\psi'}_{=:\ (\mathrm{I})} \\
+ \underbrace{2\big[\nabla_x\big(\rho^{q-1}\big)\cdot\nabla_x\psi - \nabla_x\big(\rho'^{q-1}\big)\cdot\nabla_x\psi'\big]}_{=:\ (\mathrm{II})} &+ \underbrace{\Delta_x\big(\rho^{q-1}\big)\psi - \Delta_x\big(\rho'^{q-1}\big)\psi'}_{=:\ (\mathrm{III})}\Big\},
\end{aligned} \tag{4.81}$$

which is in $\mathbb{C}^{N_{\mathrm{el}}}$. We discuss the terms one by one.

*Term (I).*
By adding and subtracting the term $\rho^{q-1}\Delta_x\psi'$ and using (4.74) with $a = q-1 > 1$, we have

$$|(\mathrm{I})| \le \big|\rho^{q-1}\big||\Delta_x\psi - \Delta_x\psi'| + \big|\rho^{q-1} - \rho'^{q-1}\big||\Delta_x\psi'| \tag{4.82}$$
$$\lesssim_q A_1|\Delta_x\psi'||\psi - \psi'| + A_2|\Delta_x\psi - \Delta_x\psi'|, \tag{4.83}$$

where

$$A_1 = \|\rho\|_{L^\infty}^{q-3/2} + \|\rho'\|_{L^\infty}^{q-3/2}, \qquad A_2 = \|\rho\|_{L^\infty}^{q-1}.$$

*Term (II).*
By adding and subtracting the term $\nabla_x\big(\rho^{q-1}\big)\cdot\nabla_x\psi'$,

$$\big|\nabla_x\big(\rho^{q-1}\big)\cdot\nabla_x\psi - \nabla_x\big(\rho'^{q-1}\big)\cdot\nabla_x\psi'\big| \le \tag{4.84}$$
$$\le \big|\nabla_x\big(\rho^{q-1}\big)\big||\nabla_x\psi - \nabla_x\psi'| + |\nabla_x\psi'|\big|\nabla_x\big(\rho^{q-1}\big) - \nabla_x\big(\rho'^{q-1}\big)\big|.$$

We get

$$\big|\nabla_x\big(\rho^{q-1}\big)\big| = (q-1)\big|\rho^{q-2}\big||\nabla_x\rho| \overset{(4.76)}{\lesssim} (q-1)\|\rho\|_{L^\infty}^{q-3/2}|\nabla_x\psi|.$$

Using this and (4.75) for $b = q-1 > 2$, we have

$$|(\mathrm{II})| \lesssim_q \big(B_1|\nabla_x\psi||\nabla_x\psi'| + B_2|\nabla_x\psi'|^2\big)|\psi - \psi'|$$
$$+ (B_3|\nabla_x\psi| + B_4|\nabla_x\psi'|)|\nabla_x\psi - \nabla_x\psi'|, \tag{4.85}$$

where

$$B_1 = \|\rho\|_{L^\infty}^{q-2}, \quad B_2 = \big\|\rho'\big\|_{L^\infty}^{1/2}\big(\|\rho\|_{L^\infty}^{q-5/2} + \|\rho'\|_{L^\infty}^{q-5/2}\big), \quad B_3 = \|\rho\|_{L^\infty}^{q-3/2},$$
$$B_4 = \|\rho\|_{L^\infty}^{q-2}\|\rho'\|_{L^\infty}^{1/2}.$$

*Term (III).*
By adding and subtracting the term $\Delta_x\big(\rho^{q-1}\big)\psi'$,

$$|(\mathrm{III})| \le \underbrace{\big|\Delta_x\big(\rho^{q-1}\big)\big|}_{=:\,(\mathrm{a})}|\psi - \psi'| + \underbrace{\big|\Delta_x\big(\rho^{q-1}\big) - \Delta_x\big(\rho'^{q-1}\big)\big|}_{=:\,(\mathrm{b})}\|\rho'\|_{L^\infty}^{1/2}.$$

We have, using $\Delta_x\rho = \overline{\psi}\cdot\Delta_x\psi + \overline{\Delta_x\psi}\cdot\psi + 2|\nabla_x\psi|^2$ and the Cauchy–Schwarz inequality,

$$|\Delta_x\rho| \lesssim \|\rho\|_{L^\infty}^{1/2}|\Delta_x\psi| + |\nabla_x\psi|^2. \tag{4.86}$$

Using this, we get

$$\begin{aligned}(\mathrm{a}) &\lesssim_q (q-2)|\rho|^{q-3}|\nabla_x\rho|^2 + |\rho|^{q-2}|\Delta_x\rho| \\ &\overset{(4.76)}{\lesssim} \|\rho\|_{L^\infty}^{q-2}\big[(2q-3)|\nabla_x\psi|^2 + \|\rho\|_{L^\infty}^{1/2}|\Delta_x\psi|\big].\end{aligned}$$

By similar reasoning, we get, by adding and subtracting the terms $\rho^{q-3}|\nabla_x\rho'|^2$ and $\rho^{q-2}\Delta_x\rho'$,

$$\begin{aligned}(\mathrm{b}) \lesssim_q (q-2)\big(|\rho|^{q-3}&\underbrace{\big||\nabla_x\rho|^2 - |\nabla_x\rho'|^2\big|}_{=:\,(\mathrm{i})} + \underbrace{\big|\rho^{q-3} - \rho'^{q-3}\big||\nabla_x\rho'|^2\big)}_{=:\,(\mathrm{ii})} \\ + |\rho|^{q-2}&\underbrace{|\Delta_x\rho - \Delta_x\rho'|}_{=:\,(\mathrm{iii})} + \underbrace{\big|\rho^{q-2} - \rho'^{q-2}\big||\Delta_x\rho'|}_{=:\,(\mathrm{iv})}.\end{aligned}$$

Using (4.76) for $\rho$ and $\rho'$, we get

$$\begin{aligned}(\mathrm{i}) &\leq (|\nabla_x\rho| + |\nabla_x\rho'|)|\nabla_x\rho - \nabla_x\rho'| \\ &\overset{(4.77)}{\lesssim} \big(\|\rho\|_{L^\infty}^{1/2}|\nabla_x\psi| + \|\rho'\|_{L^\infty}^{1/2}|\nabla_x\psi'|\big)\times \\ &\qquad \times \big(|\psi-\psi'||\nabla_x\psi| + \|\rho'\|_{L^\infty}^{1/2}|\nabla_x\psi - \nabla_x\psi'|\big).\end{aligned}$$

Using (4.74) with $a = q-3 \geq 1/2$[1] and (4.76) for $\rho'$, we have

$$(\mathrm{ii}) \lesssim_q \big(\|\rho\|_{L^\infty}^{q-7/2} + \|\rho'\|_{L^\infty}^{q-7/2}\big)\|\rho'\|_{L^\infty}|\nabla_x\psi'|^2|\psi-\psi'|.$$

In addition, by adding and subtracting the terms $\overline{\psi'}\cdot\Delta_x\psi$ and $\overline{\Delta_x\psi}\cdot\psi'$, using the reverse triangle and the Cauchy–Schwarz inequalities, we have

$$\begin{aligned}(\mathrm{iii}) =&\Big|2\big(|\nabla_x\psi|^2 - |\nabla_x\psi'|^2\big) + \big(\overline{\psi} - \overline{\psi'}\big)\cdot\Delta_x\psi + (\Delta_x\psi - \Delta_x\psi')\cdot\overline{\psi'} \\ &+ (\psi-\psi')\cdot\overline{\Delta_x\psi} + \big(\overline{\Delta_x\psi} - \overline{\Delta_x\psi'}\big)\cdot\psi'\Big| \\ \lesssim\ &(|\nabla_x\psi| + |\nabla_x\psi'|)|\nabla_x\psi - \nabla_x\psi'| + |\Delta_x\psi||\psi-\psi'| \\ &+ \|\rho'\|_{L^\infty}^{1/2}|\Delta_x\psi - \Delta_x\psi'|. \qquad (4.87)\end{aligned}$$

Furthermore, using (4.74) with $a = q-2 > 1$ and (4.86) for $\rho'$, we obtain

$$(\mathrm{iv}) \lesssim_q \big(\|\rho\|_{L^\infty}^{q-5/2} + \|\rho'\|_{L^\infty}^{q-5/2}\big)\big(\|\rho'\|_{L^\infty}^{1/2}|\Delta_x\psi'| + |\nabla_x\psi'|^2\big)|\psi-\psi'|.$$

[1] It is exactly this point in the proof that causes the restriction for the exponent in the exchange term $q \geq 7/2$ to appear.

Altogether, we get

$$
\begin{aligned}
&|(\mathrm{III})| \lesssim_q \\
&\lesssim_q \big(C_1|\nabla_x\psi|^2 + C_2|\nabla_x\psi||\nabla_x\psi'| + C_3|\nabla_x\psi'|^2 + C_4|\Delta_x\psi| + C_5|\Delta_x\psi'|\big) \\
&\quad \times |\psi-\psi'| + (C_6|\nabla_x\psi| + C_7|\nabla_x\psi'|)|\nabla_x\psi - \nabla_x\psi'| \\
&\quad + C_8|\Delta_x\psi - \Delta_x\psi'|,
\end{aligned} \tag{4.88}
$$

where

$$
\begin{aligned}
&C_1 = \|\rho\|_{L^\infty}^{q-5/2}\big(\|\rho\|_{L^\infty}^{1/2} + \|\rho'\|_{L^\infty}^{1/2}\big), \quad C_2 = \|\rho\|_{L^\infty}^{q-3}\|\rho'\|_{L^\infty}, \\
&C_3 = \|\rho'\|_{L^\infty}\big[\|\rho\|_{L^\infty}^{q-7/2}(1+\|\rho\|_{L^\infty}) + \|\rho'\|_{L^\infty}^{q-7/2}(1+\|\rho'\|_{L^\infty})\big], \\
&C_4 = \|\rho\|_{L^\infty}^{q-3/2}\big(\|\rho\|_{L^\infty}^{1/2}\|\rho'\|_{L^\infty}^{1/2} + 1\big), C_5 = \|\rho'\|_{L^\infty}\big(\|\rho\|_{L^\infty}^{q-5/2} + \|\rho'\|_{L^\infty}^{q-5/2}\big), \\
&C_6 = \|\rho\|_{L^\infty}^{q-5/2}\|\rho'\|_{L^\infty}^{1/2}\big(\|\rho\|_{L^\infty}^{1/2} + \|\rho'\|_{L^\infty}^{1/2}\big), \\
&C_7 = \|\rho\|_{L^\infty}^{q-3}\|\rho'\|_{L^\infty}^{1/2}(\|\rho\|_{L^\infty} + \|\rho'\|_{L^\infty}), \quad C_8 = \|\rho\|_{L^\infty}^{q-2}\|\rho'\|_{L^\infty}.
\end{aligned}
$$

*Conclusion of the proof of* (4.79).
The function $\mathcal{L}$ can be split into terms $\mathcal{L} = \mathcal{L}_0 + \mathcal{L}_{\mathrm{I}} + \mathcal{L}_{\mathrm{II}} + \mathcal{L}_{\mathrm{III}}$. As discussed at the start of this proof, $\mathcal{L}_0$ is the contribution of estimate (4.78) for $p = 2$. The other terms stem from (I), (II) and (III) in (4.81), and are obtained taking the $L^2$ norm in (4.83), (4.85) resp. (4.88). Here, we only discuss the $\mathcal{L}_{\mathrm{III}}$ term; all scalars $C_i$ can be bounded using (4.80). The same embedding, of $H^2$ into $L^\infty$, is also used for the factors $|\psi-\psi'|$ in the $C_1, \dots, C_5$ terms. In the $C_1$ and $C_3$ terms, also the $L^4$ integrability of the gradient terms $|\nabla_x\psi_k|$, together with the embedding of $H^1$ into $L^4$, is used; after using Young's inequality for products (A.14), the $C_2$ term follows the same line. For the $C_4$ and $C_5$ term, we use the $L^2$ integrability of the Laplacian term $|\Delta_x\psi|$. For the $C_6$ and $C_7$ terms, we use the Cauchy–Schwarz inequality, and the $C_8$ term follows by definition of the $H^2$ norm. The terms $\mathcal{L}_{\mathrm{I}}$ and $\mathcal{L}_{\mathrm{II}}$ can be handled similarly, and this concludes the proof. □

**Lemma 4.19** (Lipschitz estimates for the nonlinearity)**.** *For $q \geq 7/2$ and any $\lambda \in \mathbb{R}$, there exists a function $\mathscr{L}_{q,\lambda} : \mathbb{R}_0^+ \longrightarrow \mathbb{R}_0^+$, strictly increasing near the origin, such that for all $\psi, \psi' \in \mathcal{B}_{\mathrm{el}}(\tau)$*

$$
\begin{aligned}
&\|\mathcal{V}_{HX}[\rho]\psi - \mathcal{V}_{HX}[\rho']\psi'\|_{C^0([0,\tau];H^2)} \leq \\
&\quad \leq \mathscr{L}_{q,\lambda}\big(\alpha(\tau) + \|\psi^0\|_{H^2}\big)\|\psi-\psi'\|_{C^0([0,\tau];H^2)},
\end{aligned} \tag{4.89}
$$

$$
\|\mathcal{V}_{HX}[\rho]\psi\|_{C^0([0,\tau];H^2)} \leq \big(\alpha(\tau) + \|\psi^0\|_{H^2}\big)\mathscr{L}_{q,\lambda}\big(\alpha(\tau) + \|\psi^0\|_{H^2}\big). \tag{4.90}
$$

*Proof.* This is primarily based on the previous Lemmas: combining the estimates (4.65) from Lemma 4.15 and (4.79) from Lemma 4.18, we have that the mapping $\psi \longmapsto \mathcal{V}_{\mathrm{HX}}[\rho]\psi$ is locally Lipschitz continuous in $H^2$. Consequentially, for all $\psi, \psi' \in C^0\big([0,\tau]; H^2\big)$

$$\begin{aligned}&\|\mathcal{V}_{\mathrm{HX}}[\rho]\psi - \mathcal{V}_{\mathrm{HX}}[\rho']\psi'\|_{C^0([0,\tau];H^2)} \leq \\ &\leq \mathscr{L}_{q,\lambda}(\max\{\|\psi\|_{C^0([0,\tau];H^2)}, \|\psi'\|_{C^0([0,\tau];H^2)}\})\|\psi - \psi'\|_{C^0([0,\tau];H^2)},\end{aligned} \tag{4.91}$$

where $\mathscr{L}_{q,\lambda}$ can be created using the previously established bounds. Since this function is non-decreasing, we get (4.89) from (4.91) by definition of $\mathcal{B}_{\mathrm{el}}(\tau)$. In particular, we get (4.90) from (4.91) when we first set $\psi' \equiv 0$. □

## 4.6 Existence and uniqueness of nuclear configurations

In this section, we prove a local-in-time existence and uniqueness result for the Cauchy problem associated with (4.1b) for given $\psi \in \mathcal{B}_{\mathrm{el}}(\tau)$:

$$\ddot{X}_K = \frac{Z_K}{M_K}\Big[\int \frac{x - X_K}{|x - X_K|^3}\rho(x)\mathrm{d}x + \sum_{L=1, L\neq K}^{N_{\mathrm{nuc}}} Z_L \frac{X_K - X_L}{|X_K - X_L|^3}\Big], \tag{4.92a}$$

$$X(0) = X^0, \qquad \dot{X}(0) = V(0), \tag{4.92b}$$

with $X^0, V^0 \in \mathbb{R}^{3N_{\mathrm{nuc}}}$ such that $X^0_K \neq X^0_L$ for $1 \leq K \neq L \leq N_{\mathrm{nuc}}$.

**Lemma 4.20.** *There exists $\tau > 0$ such that the following properties hold. For given $\psi \in \mathcal{B}_{\mathrm{el}}(\tau)$, the system (4.92) has a unique short-time solution $X \in \mathcal{B}_{\mathrm{nuc}}(\tau) \cap C^2\big([0,\tau]; B_\delta\big(X^0\big)\big)$. The mapping*

$$\mathcal{N} : \psi \in \mathcal{B}_{\mathrm{el}}(\tau) \longmapsto X \in \mathcal{B}_{\mathrm{nuc}}(\tau) \cap C^2\big([0,\tau]; \mathbb{R}^{3N_{\mathrm{nuc}}}\big) \tag{4.93}$$

*is bounded in the $C^1\big([0,\tau]; \mathbb{R}^{3N_{\mathrm{nuc}}}\big)$ norm, and continuous as a map from $C^0\big([0,\tau]; L^2\big)$ to $C^0\big([0,\tau]; \mathbb{R}^{3N_{\mathrm{nuc}}}\big)$.*

*Proof. Part 1: Existence and uniqueness of $X$ in $C^2\big([0,\tau]; B_\delta\big(X^0\big)\big)$.* Since $\psi$ and so $\rho$ are given, we write the right-hand side function of (4.92a), using the acceleration function $A$ as in (3.8), but without parameters for now: $A = A(t, X)$. Note that $t$ is an explicit variable for

the $A_K^1$ terms, but not for the $A_K^2$ terms.

We define the compact set

$$\varkappa(\tau) := [0,\tau] \times B_\delta(X^0). \tag{4.94}$$

Note that we drop the dependence of this set on $\tau$. By the reverse triangle inequality, we have for all $X \in B_\delta\big(X^0\big)$ and $K = 1, \dots, N_{\mathrm{nuc}}$

$$|X_K| \leq |X| \leq \big|X^0\big| + \big|X - X^0\big| \leq \big|X^0\big| + \delta(\tau). \tag{4.95}$$

First, we prove $A$ is continuous in $(t, X)$ on $\varkappa$. To this end, we pick a sequence $\{(t_n, X_n)\}_{n\in\mathbb{N}} \subset \varkappa$ with $(t_n, X_n) \xrightarrow{n\longrightarrow\infty} (t^*, X) \in \varkappa$. The functions $A_K^1$ give for all $n$, using the Cauchy–Schwarz and Hardy's inequalities (A.4),

$$\begin{aligned}
&|A_K^1(t_n, X_n) - A_K^1(t^*, X_n)| \lesssim \\
&\lesssim \sum_{k=1}^{N_{\mathrm{el}}} \big(|X_{nK} - \cdot|^{-2}, \big|\big[\psi_k(t_n,\cdot)\big]^2 - \big[\psi_k(t^*,\cdot)\big]^2\big|\big)_{L^2} \\
&\lesssim \sum_{k=1}^{N_{\mathrm{el}}} \Big(|X_{nK} - \cdot|^{-1} \max_{t\in[0,\tau]} |\psi_k(t,\cdot)|, |X_{nK} - \cdot|^{-1} |\psi_k(t_n,\cdot) - \psi_k(t^*,\cdot)|\Big)_{L^2} \\
&\lesssim \sum_{k=1}^{N_{\mathrm{el}}} \|\nabla_x \psi_k\|_{L^\infty\left([0,\tau];L^2\right)} \|\nabla_x \psi_k(t_n,\cdot) - \nabla_x \psi_k(t^*,\cdot)\|_{L^2} \xrightarrow{n\longrightarrow\infty} 0,
\end{aligned}$$

as $\psi \in C^0\big([0,\tau]; H^1\big)$. Using this and Lemma 4.11, by which $A_K^1(t^*,\cdot) \in C^0(\mathbb{R}^{3N_{\mathrm{nuc}}}; \mathbb{C}^3)$, we have for all $n$

$$\begin{aligned}
&|A_K^1(t_n, X_n) - A_K^1(t^*, X)| \leq \\
&\leq |A_K^1(t_n, X_n) - A_K^1(t^*, X_n)| + |A_K^1(t^*, X_n) - A_K^1(t^*, X)| \xrightarrow{n\longrightarrow\infty} 0.
\end{aligned} \tag{4.96}$$

The functions $A_K^2$ are not explicitly time-dependent and continuous on $B_\delta\big(X^0\big)$, hence on $\varkappa$.

Since $A$ is continuous on the compact set $\varkappa$, it is also uniformly bounded on $\varkappa$. By Lemma 4.11,

$$\|A_K^1\|_{C^0([0,\tau];W^{1,\infty}(B_\delta(X^0);\mathbb{C}^3))} \lesssim \|\psi\|^2_{C^0([0,\tau];H^2)}, \tag{4.97}$$

since $\psi \in \mathcal{B}_{\mathrm{el}}(\tau)$. The functions $A_K^2$ are bounded on $B_\delta\big(X^0\big)$ by

$$\|A_K^2\|_{L^\infty(B_\delta(X^0);\mathbb{C}^3)} \lesssim \sum_{\substack{L=1,\\ L\neq K}}^{N_{\mathrm{nuc}}} \left\| \frac{1}{|X_K - X_L|^2} \right\|_{L^\infty(B_\delta(X^0))}. \tag{4.98}$$

Furthermore, by Lemma 4.11, $A_K^1(t,\cdot)$ is uniformly Lipschitz continuous for all $t \in [0,\tau]$ and $K$, as

$$\|DA_K^1(t,\cdot)\|_{L^\infty(\mathbb{R}^3;\mathbb{C}^{3\times 3})} \lesssim \sum_{k=1}^{N_{\mathrm{el}}} \|Df_K^{kk}(t,\cdot)\|_{L^\infty} \lesssim \|\psi\|^2_{C^0([0,\tau];H^2)} \tag{4.99}$$

since $\psi \in \mathcal{B}_{\mathrm{el}}(\tau)$. For the $A_K^2$ terms, we note that the functions $X \longmapsto (X_K - X_L)|X_K - X_L|^{-3}$ are locally Lipschitz on $B_\delta\big(X^0\big)$. Therefore, $A$ is Lipschitz continuous in $X \in B_\delta\big(X^0\big)$ and uniformly in $t \in [0,\tau]$. We denote the corresponding Lipschitz constant by $C_{\mathrm{L}}$, dropping its dependence on $\tau$.

Now, we define $\mathcal{T}$ as the following mapping on the complete metric space $C^0\big([0,\tau];B_\delta\big(X^0\big)\big)$, equipped with the $C^0\big([0,\tau];\mathbb{R}^{3N_{\mathrm{nuc}}}\big)$ norm:

$$\mathcal{T}[X](t) := X^0 + V^0 t + \int_0^t (t-\sigma) A(\sigma, X(\sigma)) \mathrm{d}\sigma. \tag{4.100}$$

By the boundedness of $A$, we have for all $X \in C^0\big([0,\tau];B_\delta\big(X^0\big)\big)$

$$\big\|\mathcal{T}[X] - X^0\big\|_{C^0([0,\tau])} \leq \big|V^0\big|\tau + \frac{\tau^2}{2}\|A\|_{C^0(\varkappa)}. \tag{4.101}$$

Note that $\mathcal{T}$ maps $C^0\big([0,\tau];B_\delta\big(X^0\big)\big)$ into itself, as for $\tau > 0$ small enough it holds that

$$\big|V^0\big|\tau + \frac{\tau^2}{2}\|A\|_{C^0(\varkappa;\mathbb{C}^{3N_{\mathrm{nuc}}})} \leq \delta(\tau). \tag{4.102}$$

Hence, for all $X, X' \in C^0([0,\tau];B_\delta\big(X^0\big))$, we have

$$\begin{aligned} &\|\mathcal{T}[X] - \mathcal{T}[X']\|_{C^0\left([0,\tau];\mathbb{R}^{3N_{\mathrm{nuc}}}\right)} \leq \\ &\quad \leq \max_{t\in[0,\tau]} \int_0^t (t-\sigma)|A(\sigma,X(\sigma)) - A(\sigma,X'(\sigma))|\mathrm{d}\sigma \\ &\quad \leq \frac{C_{\mathrm{L}}\tau^2}{2}\|X - X'\|_{C^0([0,\tau])}, \end{aligned} \tag{4.103}$$

Note also that $\mathcal{T}$ is a strict contraction on $C^0\big([0,\tau];B_\delta\big(X^0\big)\big)$ in the $C^0([0,\tau])$ norm, as we can always shrink $\tau>0$ so that

$$\frac{C_{\mathrm{L}}\tau^2}{2}<1 \tag{4.104}$$

holds. By the contraction mapping theorem, $\mathcal{T}$ has a unique fixed point in $C^0([0,\tau];B_\delta\big(X^0\big))$. Because of this, (4.92) has a unique short-time solution in $C^2\big([0,\tau];B_\delta\big(X^0\big)\big)$.

*Part 2: Localisation of $X$ in $\mathcal{B}_{\mathrm{nuc}}(\tau)$.*
Integrating the ODE in (4.92a), we get

$$\big\|\dot{X}\big\|_{C^0([0,\tau])}\leq\big|V^0\big|+\tau\|A\|_{C^0(\varkappa)}.$$

Note that $X\in\mathcal{B}_{\mathrm{nuc}}(\tau)$, picking $\tau>0$ smaller if necessary, so that

$$\tau\|A\|_{C^0(\varkappa;\mathbb{C}^{3N_{\mathrm{nuc}}})}\leq 1, \tag{4.105}$$

holds. Therefore, $X\in\mathcal{B}_{\mathrm{nuc}}(\tau)\cap C^2\big([0,\tau];B_\delta\big(X^0\big)\big)$.

*Part 3: Boundedness and continuity of $\mathcal{N}$.*
From (4.95,4.46), we have that $\mathcal{N}$ is bounded in the $C^1([0,\tau])$ norm:

$$\|X\|_{C^1([0,\tau])}\leq\big|X^0\big|+\delta(\tau)+\gamma.$$

In order to prove continuity of $\mathcal{N}$ as a map from $C^0\big([0,\tau];L^2\big)$ to $C^0\big([0,\tau];\mathbb{R}^{3N_{\mathrm{nuc}}}\big)$, we consider a sequence $\{\psi_n\}_{n\in\mathbb{N}}\subset\mathcal{B}_{\mathrm{el}}(\tau)$ such that $\psi_n\xrightarrow{n\longrightarrow\infty}\psi\in\mathcal{B}_{\mathrm{el}}(\tau)$ in the $C^0\big([0,\tau];L^2\big)$ norm. Similarly to $X=\mathcal{N}[\psi]$, we define $X_n:=\mathcal{N}[\psi_n]$ and $\rho_n:=|\psi_n|^2$. Note that $X$ and $X_n$ are fixed points of the mapping $\mathcal{T}$ introduced in Part 1 of the proof. Using this, for all $t\in[0,\tau]$

$$|(X_n-X)(t)|\leq\int_0^t(t-\sigma)|A[\rho_n](X(\sigma))-A[\rho](X(\sigma))|\mathrm{d}\sigma, \tag{4.106}$$

where

$$|A[\rho_n](X_n(\sigma))-A[\rho](X(\sigma))|\leq$$
$$\leq\underbrace{\sum_{K=1}^{N_{\mathrm{nuc}}}|A_K^1[\rho_n](X_n(\sigma))-A_K^1[\rho](X(\sigma))|}_{=:(\mathrm{I})}+\underbrace{\sum_{K=1}^{N_{\mathrm{nuc}}}|A_K^2(X_n(\sigma))-A_K^2(X(\sigma))|}_{=:(\mathrm{II})}.$$

We have

$$\begin{aligned}
&\text{(I)} \lesssim \text{(Ia)} + \text{(Ib)},\\
&\text{(Ia)} := \sum_{k=1}^{N_{\mathrm{el}}} |(\psi_k(t,\cdot), \Xi(\cdot - X_K)(\psi_{nk}(t,\cdot) - \psi_k(t,\cdot)))_{L^2}\\
&\qquad + (\psi_{nk}(t,\cdot) - \psi_k(t,\cdot), \Xi(\cdot - X_{nK})\psi_{nk}(t,\cdot))_{L^2}|,\\
&\text{(Ib)} := \sum_{k=1}^{N_{\mathrm{el}}} |(\psi_k(t,\cdot), \Xi(\cdot - X_{nK})\psi_{nk}(t,\cdot))_{L^2}\\
&\qquad - (\psi_k(t,\cdot), \Xi(\cdot - X_K)\psi_{nk}(t,\cdot))_{L^2}|,
\end{aligned}$$

where $\Xi(x) := x\|x\|_{\mathbb{R}^3}^{-3}$. Arguing as in [CB99, p. 980], (Ia) can be bounded by

$$\begin{aligned}
\beta_n := \sum_{k=1}^{N_{\mathrm{el}}} &\sup_{(t,x)\in[0,\tau]\times\mathbb{R}^3} \big(|\cdot - x|^{-1}|\psi_k(t,\cdot) + \psi_{nk}(t,\cdot)|,\\
&|\cdot - x|^{-1}|\psi_{nk}(t,\cdot) - \psi_k(t,\cdot)|\big)_{L^2} \xrightarrow{n\longrightarrow\infty} 0,
\end{aligned}$$

as $\psi_n \xrightarrow{n\longrightarrow\infty} \psi$ in $C^0\big([0,\tau]; L^2\big)$. We also have

$$\begin{aligned}
\text{(Ib)} &\lesssim \sum_{k=1}^{N_{\mathrm{el}}} \|\nabla_x G[\psi_k, \psi_{nk}](X_{nK}) - \nabla_x G[\psi_k, \psi_{nk}](X_K)\|_{C^0([0,\tau];\mathbb{C}^3)}\\
&\leq C^{\mathrm{L}}_{1,n}|X_n - X|,
\end{aligned}$$

where we adopted the map $G$ from (4.21), and used that the functions $\nabla_x G[\psi_k, \psi_{nk}]$ are uniformly Lipschitz continuous in $X$ for uniformly all $t \in [0,\tau]$. So is (II), with some Lipschitz constant $C^{\mathrm{L}}_{2,n}$. For all $n$, $C^{\mathrm{L}}_{1,n}$ and $C^{\mathrm{L}}_{2,n}$ are uniformly bounded by $C^{\mathrm{L}}$, since all $\psi_n$ and $\psi$ are taken from the uniformly bounded set $\mathcal{B}_{\mathrm{el}}(\tau)$. Altogether, from (4.106) we obtain

$$\|X_n - X\|_{C^0([0,\tau])} \lesssim \tau^2\|X_n - X\|_{C^0([0,\tau])} + \tau^2\beta_n.$$

It is then clear that for $\tau$ small enough the conclusion follows. □

## 4.7 Existence and uniqueness of electronic configurations

In this section, we prove a local-in-time existence and uniqueness result for the Cauchy problem associated with (4.1b) for given $X \in \mathcal{B}_{\mathrm{nuc}}(\tau)$:

$$i\dot{\psi}_k = -\tfrac{1}{2}\Delta_x\psi_k - \sum_{K=1}^{N_{\mathrm{nuc}}} \frac{Z_K}{|\cdot - X_K|}\psi_k + \left(\frac{1}{|\cdot|} * \rho\right)\psi_k + \lambda\rho^{q-1}\psi_k, \quad (4.107a)$$

$$\psi(0) = \psi^0 \quad (4.107b)$$

with $\psi^0 \in H^2$.

**Lemma 4.21.** *Let $q \geq 7/2$, $\lambda \in \mathbb{R}$. Then, there exists $\tau > 0$ such that the following holds. For given $X \in \mathcal{B}_{\mathrm{nuc}}(\tau)$, the system (4.107) has a unique short-time solution $\psi$ in $\mathcal{B}_{\mathrm{el}}(\tau)$.*

*Proof.* This proof is based on Lemma 4.12, which ensures the existence and the $\mathcal{L}(H^2)$ bounds of the propagator $U(t,s)$ for the family of linear Hamiltonians $\{H^{\mathrm{KS,lin}}(t), t \in [0,\tau]\}$ from (4.33), and on Lemma 4.19, which ensures that the nonlinear mapping $\psi \longmapsto \mathcal{V}_{\mathrm{HX}}[\rho]\psi$ is locally Lipschitz in $H^2$.

We define $\mathcal{F}$ as the following mapping on the complete metric space $C^0\big([0,\tau]; B_\alpha(\psi^0)\big)$, equipped with the $C^0\big([0,\tau]; H^2\big)$ norm:

$$(\mathcal{F}[\psi])(t) := U(t,0)\psi^0 - i\int_0^t U(t,\sigma)\mathcal{V}_{\mathrm{HX}}[\rho]\psi(\sigma)\mathrm{d}\sigma,$$

with $\mathcal{V}_{\mathrm{HX}}$ as defined in (4.62). Note that we obtain for all $\psi \in C^0\big([0,\tau]; B_\alpha(\psi^0)\big)$, using Lemma 4.12, property 2,

$$\mathcal{F}[\psi](0) = U(0,0)\psi^0 = \psi^0. \quad (4.108)$$

Note also that, provided that

$$\big[1 + B_{\tau,\gamma} + \tau B_{\tau,\gamma}(2B_{\tau,\gamma}+1)\mathscr{L}_{q,\lambda}\big(\alpha + \big\|\psi^0\big\|_{H^2}\big)\big] \leq 2B_{\tau,\gamma}, \quad (4.109)$$

we have that $\mathcal{F}$ maps the complete metric space $C^0\big([0,\tau]; B_\alpha(\psi^0)\big)$ into

itself, as

$$\begin{aligned}
&\left\|\mathcal{F}[\psi]-\psi^0\right\|_{C^0([0,\tau];H^2)} = \\
&= \left\|[U(\cdot,0)-\mathrm{Id}]\psi^0 - i\int_0^{\cdot} U(\cdot,\sigma)\mathcal{V}_{\mathrm{HX}}[\rho]\psi(\sigma)\mathrm{d}\sigma\right\|_{C^0([0,\tau];H^2)} \\
&\leq B_{\tau,\gamma}\left(\left\|\psi^0\right\|_{H^2} + \tau\|\mathcal{V}_{\mathrm{HX}}[\rho]\psi\|_{C^0([0,\tau];H^2)}\right) + \left\|\psi^0\right\|_{H^2} \qquad (4.110)\\
&\overset{(4.90)}{\leq} \left[1 + B_{\tau,\gamma} + \tau B_{\tau,\gamma}(2B_{\tau,\gamma}+1)\mathscr{L}_{q,\lambda}\left(\alpha + \left\|\psi^0\right\|_{H^2}\right)\right]\left\|\psi^0\right\|_{H^2} \\
&\overset{(4.109)}{\leq} 2B_{\tau,\gamma}\left\|\psi^0\right\|_{H^2} = \alpha,
\end{aligned}$$

where we used Lemma 4.12, property 8 in (4.110). Moreover, note that, provided that

$$\tau B_{\tau,\gamma}\mathscr{L}_{q,\lambda}\left(\alpha(\tau) + \left\|\psi^0\right\|_{H^2}\right) < 1, \qquad (4.111)$$

we have that $\mathcal{F}$ is a contraction on $C^0\left([0,\tau];B_\alpha\left(\psi^0\right)\right)$ in the $C^0\left([0,\tau];H^2\right)$ norm, as for all $\psi,\psi' \in C^0\left([0,\tau];B_\alpha\left(\psi^0\right)\right)$

$$\begin{aligned}
&\|\mathcal{F}[\psi]-\mathcal{F}[\psi']\|_{C^0([0,\tau];H^2)} = \\
&= \left\|\int_0^{\cdot} U(\cdot,\sigma)(\mathcal{V}_{\mathrm{HX}}[\rho]\psi(\sigma) - \mathcal{V}_{\mathrm{HX}}[\rho']\psi'(\sigma))\mathrm{d}\sigma\right\|_{C^0([0,\tau];H^2)} \\
&\leq \tau B_{\tau,\gamma}\|\mathcal{V}_{\mathrm{HX}}[\rho]\psi - \mathcal{V}_{\mathrm{HX}}[\rho']\psi'\|_{C^0([0,\tau];H^2)} \qquad (4.112)\\
&\overset{(4.89)}{\leq} \tau B_{\tau,\gamma}\mathscr{L}_{q,\lambda}\left(\alpha + \left\|\psi^0\right\|_{H^2}\right)\|\psi-\psi'\|_{C^0([0,\tau];H^2)} \overset{(4.111)}{<} \|\psi-\psi'\|_{C^0([0,\tau];H^2)},
\end{aligned}$$

where we used Lemma 4.12, property 8 in (4.112). By the contraction mapping theorem, $\mathcal{F}$ has a unique fixed point in $C^0\left([0,\tau];B_\alpha\left(\psi^0\right)\right)$.

It is now left to prove that this fixed point, simply denoted by $\psi$, is also of class $C^1\left([0,\tau];L^2\right)$; then, it solves (4.107) strongly on $[0,\tau]$. To this end, we consider the following identity, which holds for all $0 \leq t < t' \leq \tau$:

$$\begin{aligned}
&i\frac{\psi(t')-\psi(t)}{t'-t} = \\
&= i\frac{U(t',0)-U(t,0)}{t'-t}\psi^0 + \int_0^t \frac{U(t',\sigma)-U(t,\sigma)}{t'-t}\mathcal{V}_{\mathrm{HX}}[\rho]\psi(\sigma)\mathrm{d}\sigma \\
&\quad + \int_t^{t'} \frac{U(t',\sigma)}{t'-t}\mathcal{V}_{\mathrm{HX}}[\rho]\psi(\sigma)\mathrm{d}\sigma, \qquad (4.113)
\end{aligned}$$

and we show that

$$\|(4.113) - H^{\mathrm{KS}}[X(t),\rho]\psi(t)\|_{L^2} \xrightarrow{t'\longrightarrow t} 0,$$

where the expression (4.113) involves all three integral terms. This will imply that $\psi(\cdot)$ is differentiable as a mapping $[0,\tau] \longmapsto L^2$ with a derivative $\dot{\psi}(\cdot)$ such that

$$i\dot{\psi}(t) = H^{\mathrm{KS}}[X(t),\rho]\psi(t).$$

Note, in particular, that for the given $X \in \mathcal{B}_{\mathrm{nuc}}(\tau)$, $H^{\mathrm{KS}}[X(\cdot),\rho]\psi(\cdot)$ is a continuous mapping $[0,\tau] \longrightarrow L^2$, which will imply that $\psi \in C^1\big([0,\tau];L^2\big)$, so that the PDE is satisfied in the strong sense. We have

$$\begin{aligned}
&\|(4.113) - H^{\mathrm{KS}}[X(t),\rho]\psi(t)\|_{L^2} \le (\mathrm{I}) + (\mathrm{II}),\\
&(\mathrm{I}) := \Big\| i\frac{U(t',0)-U(t,0)}{t'-t}\psi^0 + \int_0^t \frac{U(t',\sigma)-U(t,\sigma)}{t'-t}\mathcal{V}_{\mathrm{HX}}[\rho]\psi(\sigma)\mathrm{d}\sigma\\
&\qquad - H^{\mathrm{KS,lin}}(t)\psi(t)\Big\|_{L^2},\\
&(\mathrm{II}) := \Big\| \int_t^{t'} \frac{U(t',\sigma)}{t'-t}\mathcal{V}_{\mathrm{HX}}[\rho]\psi(\sigma)\mathrm{d}\sigma - \mathcal{V}_{\mathrm{HX}}[\rho]\psi(t)\Big\|_{L^2}.
\end{aligned}$$

In the limit, we get

$$\begin{aligned}
&\lim_{t'\to t}\{(\mathrm{I})\} =\\
&= \Big\| i\frac{\partial}{\partial t}\big[U(t,0)\psi^0\big] + \int_0^t \frac{\partial}{\partial t}[U(t,\sigma)\mathcal{V}_{\mathrm{HX}}[\rho]\psi(\sigma)]\mathrm{d}\sigma - H^{\mathrm{KS,lin}}(t)\psi(t)\Big\|_{L^2}\\
&= \Big\| H^{\mathrm{KS,lin}}(t)\big[U(t,0)\psi^0\big] + \int_0^t -iH^{\mathrm{KS,lin}}(t)[U(t,\sigma)\mathcal{V}_{\mathrm{HX}}[\rho]\psi(\sigma)]\mathrm{d}\sigma\\
&\qquad - H^{\mathrm{KS,lin}}(t)\psi(t)\Big\|_{L^2} \qquad (4.114)\\
&= \|H^{\mathrm{KS,lin}}(t)[\mathcal{F}[\psi(t)] - \psi(t)]\|_{L^2} = 0, \qquad (4.115)
\end{aligned}$$

where we used Lemma 4.12, property 7 (see also [Yaj87, Thm. 1.3. (6)]) in (4.114), the linearity of the Hamiltonians $H^{\mathrm{KS,lin}}(t)$ and $\psi$ being a

fixed point of $\mathcal{F}$ in (4.115). We also have

$$\text{(II)} \leq \underbrace{\left\| \frac{1}{t'-t} \int_t^{t'} U(t,\sigma)\mathcal{V}_{\mathrm{HX}}[\rho]\psi(\sigma)\mathrm{d}\sigma - \mathcal{V}_{\mathrm{HX}}[\rho]\psi(t) \right\|_{L^2}}_{=:\text{(a)}}$$
$$+ \underbrace{\frac{1}{t'-t} \left\| \int_t^{t'} [U(t',\sigma) - U(t,\sigma)]\mathcal{V}_{\mathrm{HX}}[\rho]\psi(\sigma)\mathrm{d}\sigma \right\|_{L^2}}_{=:\text{(b)}}.$$

In the limit, (a) goes to zero, because of the fundamental theorem of calculus for Bochner integrals and Lemma 4.12, property 2. Furthermore, we have

$$\begin{aligned} \lim_{t'\to t}\{\text{(b)}\} &\leq \lim_{t'\to t}\left\{ \frac{1}{t'-t} \int_t^{t'} \|[U(t',\sigma) - U(t,\sigma)]\mathcal{V}_{\mathrm{HX}}[\rho]\psi(\sigma)\|_{L^2}\mathrm{d}\sigma \right\} \\ &\leq \lim_{t'\to t}\{\|[U(t',\cdot) - U(t,\cdot)]\mathcal{V}_{\mathrm{HX}}[\rho]\psi\|_{C^0([0,T],L^2)}\} = 0, \end{aligned} \tag{4.116}$$

where we used the uniform continuity of $U(t,s)\mathcal{V}_{\mathrm{HX}}[\rho]\psi(s)$ on $[0,T]^2$ together with Lemma 4.12, property 4 in (4.116). Since $\psi$ also is a fixed point of $\mathcal{F}$, by which $\psi = \mathcal{F}[\psi](0) = \psi^0$ (see (4.108)), we know $\psi$ is a strong solution to (4.107) on $[0,\tau]$.

Now, we show uniqueness of the short-time solution $\psi$ to (4.107) in the class $C^1\big([0,\tau];L^2\big) \cap C^0\big([0,\tau];B_\alpha\big(\psi^0\big)\big)$: although the classical contraction mapping theorem also provides uniqueness, this is only in the class $C^0\big([0,\tau];B_\alpha\big(\psi^0\big)\big)$. So, now we prove uniqueness in the different space $C^1\big([0,\tau];L^2\big)$. To this end, we let $\psi$ and $\psi'$ be two short-time solutions of (4.107) in $C^1\big([0,\tau];L^2\big)$. First, we have $(\psi-\psi')(0) = \psi^0 - \psi^0 = 0$. Moreover, for all $k \in \{1,\dots,N_{\mathrm{el}}\}$, using the PDE in (4.107a),

$$\begin{aligned} &\frac{\mathrm{d}}{\mathrm{d}t}\|\psi_k - \psi_k'\|_{L^2}^2 = \frac{\mathrm{d}}{\mathrm{d}t}(\psi_k - \psi_k', \psi_k - \psi_k')_{L^2} \\ &= \big(\dot\psi_k - \dot\psi_k', \psi_k - \psi_k'\big)_{L^2} + \overline{\big(\dot\psi_k - \dot\psi_k', \psi_k - \psi_k'\big)_{L^2}} = \text{(I)} + \text{(II)}, \end{aligned}$$

where we have, using that the linear Hamiltonians $H^{\mathrm{KS,lin}}(t)$ are self-adjoint on $L^2$,

$$\begin{aligned} \text{(I)} = i[&(\psi_k - \psi_k', (H^{\mathrm{KS,lin}}(t)(\psi-\psi'))_k)_{L^2} \\ &- ((H^{\mathrm{KS,lin}}(t)(\psi-\psi'))_k, \psi_k - \psi_k')_{L^2}] = 0, \end{aligned}$$

and

$$\begin{aligned}
&(\mathrm{II}) = \\
&= i\Big[\overline{((\mathcal{V}_{\mathrm{HX}}[\rho]\psi - \mathcal{V}_{\mathrm{HX}}[\rho']\psi')_k, \psi_k - \psi'_k)_{L^2}} \\
&\qquad - ((\mathcal{V}_{\mathrm{HX}}[\rho]\psi - \mathcal{V}_{\mathrm{HX}}[\rho']\psi')_k, \psi_k - \psi'_k)_{L^2}\Big] \\
&= 2\mathrm{Im}((\mathcal{V}_{\mathrm{HX}}[\rho]\psi - \mathcal{V}_{\mathrm{HX}}[\rho']\psi')_k, \psi_k - \psi'_k)_{L^2}.
\end{aligned}$$

Using this, we get

$$\begin{aligned}
&\frac{\mathrm{d}}{\mathrm{d}t}\big(\|\psi - \psi'\|_{L^2}^2\big) = \sum_{k=1}^{N_{\mathrm{el}}} \frac{\mathrm{d}}{\mathrm{d}t}\big(\|\psi_k - \psi'_k\|_{L^2}^2\big) \\
&= 2\mathrm{Im}(\mathcal{V}_{\mathrm{HX}}[\rho]\psi - \mathcal{V}_{\mathrm{HX}}[\rho']\psi', \psi - \psi')_{L^2} \leq C\|\psi - \psi'\|_{L^2}^2,
\end{aligned}$$

where $C = C(\|\psi\|_{C^0([0,\tau];H^2)}, \|\psi'\|_{C^0([0,\tau];H^2)}, \tau, q, \lambda, N_{\mathrm{el}}) > 0$ stems from the Cauchy–Schwarz inequality and combining (4.63) from Lemma 4.15 and (4.78) from Lemma 4.18. Now, by Grönwall's Lemma, we get that $\psi = \psi'$.

Note that there is always $\tau > 0$ small enough such that the inequalities (4.109,4.111) are satisfied. Recall that $B_{\tau,\gamma}$ and $\alpha$ are of the form

$$B_{\tau,\gamma} = A_\gamma^{1+C_\gamma\tau} > 1, \qquad \alpha(\tau) = 2A_\gamma^{1+C_\gamma\tau}\big\|\psi^0\big\|_{H^2},$$

with $A_\gamma, C_\gamma > 1$ defined as in Lemma 4.12, property 8. Let

$$g(\tau) := \tau B_{\tau,\gamma}\frac{2B_{\tau,\gamma}+1}{B_{\tau,\gamma}-1}\mathscr{L}_{q,\lambda}\big(\alpha(\tau) + \big\|\psi^0\big\|_{H^2}\big) - 1. \tag{4.117}$$

Since $g(0) < 0$, the conclusion follows by continuity. □

**Lemma 4.22.** *Let $q \geq 7/2$ and $\lambda \in \mathbb{R}$. Let $\tau > 0$ be such that the following holds: for given $X \in \mathcal{B}_{\mathrm{nuc}}(\tau)$, $\psi \in \mathcal{B}_{\mathrm{el}}(\tau)$ is the unique short-time solution to (4.107). Then, the mapping*

$$\mathcal{E} : \psi \in \mathcal{B}_{\mathrm{nuc}}(\tau) \longmapsto X \in \mathcal{B}_{\mathrm{el}}(\tau),$$

*is bounded and continuous as map from $C^0\big([0,\tau];\mathbb{R}^{3N_{\mathrm{nuc}}}\big)$ to $C^0\big([0,\tau];L^2\big)$.*

*Proof.* Since $\mathcal{B}_{\mathrm{el}}(\tau)$ is a bounded subset of $C^0\big([0,\tau];L^2\big)$, the mapping $\mathcal{E}$ is bounded in the $C^0\big([0,\tau];L^2\big)$ norm. In order to prove continuity of $\mathcal{E}$ as map from $C^0\big([0,\tau];\mathbb{R}^{3N_{\mathrm{nuc}}}\big)$ to $C^0\big([0,\tau];L^2\big)$, we consider a sequence $\{X_n\}_{n\in\mathbb{N}} \subset \mathcal{B}_{\mathrm{nuc}}(\tau)$ such that $X_n \xrightarrow{n\longrightarrow\infty} X \in \mathcal{B}_{\mathrm{nuc}}(\tau)$ in the $C^0([0,\tau])$ norm. Similarly to $\psi = \mathcal{E}[X]$, we define $\psi_n := \mathcal{E}[X_n]$ with $\rho_n := |\psi_n|^2$. Then,

$$i\frac{\partial}{\partial t}(\psi_n - \psi) = H^{\mathrm{KS}}[X,\rho](\psi_n - \psi) + \zeta_n, \qquad (\psi_n - \psi)(0) = 0,$$

with

$$\begin{aligned}
\zeta_n &:= \zeta_n^1 + \zeta_n^2 + \zeta_n^3,\\
\zeta_n^1 &:= \mathcal{V}_{\mathrm{ext}}[X_n]\psi_n - \mathcal{V}_{\mathrm{ext}}[X]\psi - \mathcal{V}_{\mathrm{ext}}[X](\psi_n - \psi)\\
&= (\mathcal{V}_{\mathrm{ext}}[X_n] - \mathcal{V}_{\mathrm{ext}}[X])\psi_n,\\
\zeta_n^2 &:= \mathcal{V}_{\mathrm{H}}[\rho_n]\psi_n - \mathcal{V}_{\mathrm{H}}[\rho]\psi - \mathcal{V}_{\mathrm{H}}[\rho](\psi_n - \psi)\\
&= \sum_{k=1}^{N_{\mathrm{el}}} \big\{\mathrm{Re}\big[\overline{(\psi_{nk} - \psi_k)}(\psi_{nk} + \psi_k)\big] * |\cdot|^{-1}\big\}\psi_n, \qquad (4.118)\\
\zeta_n^3 &:= \mathcal{V}_{\mathrm{x}}[\rho_n]\psi_n - \mathcal{V}_{\mathrm{x}}[\rho]\psi - \mathcal{V}_{\mathrm{x}}[\rho](\psi_n - \psi) = \lambda\big(\rho_n^{q-1} - \rho^{q-1}\big)\psi_n,
\end{aligned}$$

where we used $|u|^2 - |v|^2 = \mathrm{Re}[\overline{(u-v)}(u+v)]$ in (4.118). We denote by $\{H^{\mathrm{KS}}[X(t),\rho], t\in[0,T]\}$ the family of KS Hamiltonians for the given $X \in \mathcal{B}_{\mathrm{nuc}}(\tau)$. Note that since $\psi$ and thus $\rho$ are fixed now, these Hamiltonians are acting linearly on $\psi_n - \psi$, and can thus be written, similarly to (4.33), as

$$H^{\mathrm{KS}}(t) = -\tfrac{1}{2}\Delta_x + V(t) + \mathcal{V}_{\mathrm{HX}}[\rho]$$

with $V(t,\cdot) = V_{\mathrm{ext}}[X(t)]$ as before in Section 4.3. We have that the linear potential $V(t) + \mathcal{V}_{\mathrm{HX}}[\rho]$ satisfies Assumption 4.4; hence, there exists a family of evolution operators $\{\mathfrak{U}(t,s), (t,s)\in[0,T]^2\}$, associated with this family of Hamiltonians, satisfying properties 1–4 of our Lemma 4.12.[2] In what now follows, we argue like [CH98, Lemma 4.1.1.]. For fixed $t \in (0,T]$, we consider the mapping

$$u(\sigma) := \mathfrak{U}(t,\sigma)(\psi_n - \psi)(\sigma)$$

[2]Note that these four properties are a consequence of [Yaj87, Thm. 1.1], which requires only the Assumption (A.1), stated above the mentioned Theorem.

for $\sigma \in [0,t]$. Let $\sigma \in [0,t]$ and $h \in (0, t-\sigma)$. Then, we have

$$\begin{aligned}
&\frac{u(\sigma+h)-u(\sigma)}{h} = \\
&= \tfrac{1}{h}\Big[\mathfrak{U}(t,\sigma+h)(\psi_n-\psi)(\sigma+h) - \mathfrak{U}(t,\sigma)(\psi_n-\psi)(\sigma)\Big] \\
&= \mathfrak{U}(t,\sigma+h)\tfrac{1}{h}[(\psi_n-\psi)(\sigma+h) - \mathfrak{U}(\sigma+h,\sigma)(\psi_n-\psi)(\sigma)] \qquad (4.119)\\
&= \mathfrak{U}(t,\sigma+h)\Bigg[\frac{(\psi_n-\psi)(\sigma+h)-(\psi_n-\psi)(\sigma)}{h} \\
&\qquad\qquad - \frac{\mathfrak{U}(\sigma+h,\sigma)-\mathrm{Id}}{h}(\psi_n-\psi)(\sigma)\Bigg] \\
&\xrightarrow{h\downarrow 0} \mathfrak{U}(t,\sigma)\Big[\frac{\partial}{\partial t}(\psi_n-\psi)(\sigma) + iH^{\mathrm{KS}}[X(\sigma),\rho](\psi_n-\psi)(\sigma)\Big] \qquad (4.120)\\
&= -i\mathfrak{U}(t,\sigma)\zeta_n(\sigma).
\end{aligned}$$

where we used Lemma 4.12, property 1 in (4.119) and [Yaj87, Cor. 1.2. (4)] in (4.120). Due to Lemma 4.12, property 4, we know that for fixed $t \in [0,T]$, $\mathfrak{U}(t,\cdot)\zeta_n \in C^0\big([0,T], L^2\big)$; hence, we have that $u \in C^1\big([0,t); L^2\big)$, with for all $\sigma \in [0,t)$

$$u'(\sigma) = -i\mathfrak{U}(t,\sigma)\zeta_n(\sigma).$$

Integrating this expression from 0 to $t' < t$ over $\sigma$, we obtain the expression

$$u(t') - u(0) = \mathfrak{U}(t,t')(\psi_n-\psi)(t') = -i\int_0^{t'} \mathfrak{U}(t,\sigma)\zeta_n(\sigma)\mathrm{d}\sigma.$$

In the limit $t' \longrightarrow t$, using Lemma 4.12, property 2, it follows that the corresponding integral representation holds for all $t \in [0,T]$:

$$(\psi_n-\psi)(t) = -i\int_0^{t} \mathfrak{U}(t,\sigma)\zeta_n(\sigma)\mathrm{d}\sigma.$$

Using Lemma 4.12, property 3, for all $n \in \mathbb{N}$ and $t \in [0,\tau]$

$$\|(\psi_n-\psi)(t)\|_{L^2} \lesssim \sum_{j\in\{1,2,3\}} \int_0^t \|\zeta_n^j(\sigma)\|_{L^2}\mathrm{d}\sigma.$$

So, now we deduce $L^2$ estimates on $\zeta_n^j(\sigma)$ for $j \in \{1,2,3\}$ for all $\sigma \in (0,t)$, using that $\psi_n$ and $\psi \in \mathcal{B}_{\mathrm{el}}(\tau)$, which makes them uniformly bounded with

respect to $n$ in $C^0\big([0,\tau];H^2\big)$. For $j=1$, we note that this makes them uniformly bounded with respect to $n$ in $L^\infty\big([0,\tau];L^2\big)$ and $L^\infty([0,\tau];L^\infty)$ too, using the embedding of $H^2$ into $L^\infty$. Also, we use that for all $n$, $V_{\text{ext}}[X_n(\cdot)] = V_n^1 + V_n^2$ and $V_{\text{ext}}[X(\cdot)] = V^1 + V^2$ belong to the space $C^0\big([0,T];L^2\big) + C^0([0,T];L^\infty)$, and their difference goes to zero in this space; see also (4.45). Together, this gives for all $0 < \sigma < t \leq \tau \leq T$

$$
\begin{aligned}
&\|\zeta_n^1(\sigma)\|_{L^2} \leq \\
&\leq \|(V_n^1(\sigma) - V^1(\sigma))\psi_n(\sigma)\|_{L^2} + \|(V_n^2(\sigma) - V^2(\sigma))\psi_n(\sigma)\|_{L^2} \\
&\leq \|V_n^1 - V^1\|_{L^\infty\left([0,T];L^2\right)} \|\psi_n\|_{L^\infty([0,\tau];L^\infty)} \\
&\quad + \|V_n^2 - V^2\|_{L^\infty([0,T];L^\infty)} \|\psi_n\|_{L^\infty\left([0,\tau];L^2\right)} \\
&\leq C(\|V_n^1 - V^1\|_{L^\infty\left([0,T];L^2\right)} + \|V_n^2 - V^2\|_{L^\infty([0,T];L^\infty)}) =: C_{1,n} \xrightarrow{n\longrightarrow\infty} 0
\end{aligned}
$$

for some $C = C\big(\alpha,\psi^0\big) > 0$. For $j=2$, we adopt the map $G$ from (4.21). This gives for all $\sigma \in (0,t)$

$$
\begin{aligned}
&\|\zeta_n^2(\sigma)\|_{L^2} \leq \\
&\leq \sum_{k=1}^{N_{\text{el}}} \|G[\psi_{nk}(\sigma) - \psi_k(\sigma), \psi_{nk}(\sigma) + \psi_k(\sigma)]\|_{L^\infty} \|\psi_n(\sigma)\|_{L^2} \\
&\lesssim \sum_{k=1}^{N_{\text{el}}} \|\psi_{nk}(\sigma) - \psi_k(\sigma)\|_{L^2} \|\psi_{nk}(\sigma) + \psi_k(\sigma)\|_{H^2} \|\psi_n\|_{L^\infty\left([0,\tau];L^2\right)} \\
&\leq C_2 \|\psi_n(\sigma) - \psi(\sigma)\|_{L^2}
\end{aligned}
$$

for some $C_2 = C_2\big(\alpha,\psi^0\big) > 0$. For $j=3$, we have for all $\sigma \in (0,t)$

$$
\begin{aligned}
&\|\zeta_n^3(\sigma)\|_{L^2} \overset{(4.74)}{\lesssim_{q,\lambda}} \\
&\lesssim_{q,\lambda} \big(\|\rho_n(\sigma)\|_{L^\infty}^{q-3/2} + \|\rho(\sigma)\|_{L^\infty}^{q-3/2}\big) \|\rho_n(\sigma)\|_{L^\infty}^{1/2} \|\psi_n(\sigma) - \psi(\sigma)\|_{L^2} \\
&\overset{(4.80)}{\leq} C_3 \|\psi_n(\sigma) - \psi(\sigma)\|_{L^2},
\end{aligned}
$$

for some $C_3 = C_3\big(q,\alpha,\psi^0\big) > 0$. Combining these three estimates, for all $t \in [0,\tau]$

$$
\|(\psi_n - \psi)(t)\|_{L^2} \leq C_{1,n}\tau + (C_2 + C_3) \int_0^t \|[\psi_n - \psi](\sigma)\|_{L^2} \mathrm{d}\sigma,
$$

Now, by Grönwall's inequality (A.15) we conclude that for all $t \in [0,\tau]$

$$\|(\psi_n - \psi)(t)\|_{L^2} \leq C_{1,n}\tau e^{(C_2+C_3)t}, \tag{4.121}$$

which concludes the proof. □

## 4.8 Existence and uniqueness of the coupled solution

In this section, we prove the main result, Theorem 4.1.

**Lemma 4.23.** *Let $q \geq 7/2$ and $\lambda \in \mathbb{R}$. Then, there exists $\tau > 0$ such that the system (4.1) has a solution $(\psi, X)$ in*

$$C^0\big([0,\tau]; H^2\big(\mathbb{R}^3;\mathbb{C}^{N_{\mathrm{el}}}\big)\big) \cap C^1\big([0,\tau]; L^2\big(\mathbb{R}^3;\mathbb{C}^{N_{\mathrm{el}}}\big)\big) \times C^2\big([0,\tau];\mathbb{R}^{3N_{\mathrm{nuc}}}\big).$$

*Proof.* Let $\tau > 0$ be such that the following statements hold. For given $\psi \in \mathcal{B}_{\mathrm{el}}(\tau)$, (4.92) has a unique solution $X \in \mathcal{B}_{\mathrm{nuc}}(\tau) \cap C^2\big([0,\tau]; B_\delta\big(X^0\big)\big)$, and for given $X \in \mathcal{B}_{\mathrm{nuc}}(\tau)$, (4.107) has a unique solution $\psi \in \mathcal{B}_{\mathrm{el}}(\tau)$. Existence of such $\tau$ has been proven in Lemmas 4.20 and 4.21. We define the inclusion

$$\mathcal{I} : \mathcal{B}_{\mathrm{nuc}}(\tau) \cap C^2\big([0,\tau];\mathbb{R}^{3N_{\mathrm{nuc}}}\big) \hookrightarrow \mathcal{B}_{\mathrm{nuc}}(\tau),$$

which is a continuous and compact mapping. Also, we define the mapping

$$\mathcal{K} : \mathcal{B}_{\mathrm{nuc}}(\tau) \longrightarrow \mathcal{B}_{\mathrm{nuc}}(\tau), \qquad \mathcal{K} := \mathcal{I} \circ \mathcal{N} \circ \mathcal{E}.$$

Since by Lemma 4.20, $\mathcal{N}$ is bounded in the $C^1([0,\tau])$ norm, by the Arzelà–Ascoli theorem it follows that $\mathcal{K}$ is a compact mapping, where $\mathcal{B}_{\mathrm{nuc}}(\tau)$ is equipped with the $C^0([0,\tau])$ topology.

By the classical Schauder's fixed point theorem, $\mathcal{K}$ has a fixed point $X$ in $\mathcal{B}_{\mathrm{nuc}}(\tau)$. Setting $\psi := \mathcal{E}[X]$, the corresponding pair $(\psi, X)$ is the desired solution, and this concludes the proof. □

Now, we will arrive at the uniqueness result of the solution $(\psi, X)$. To this end, we prove the following Lemma.

**Lemma 4.24.** *Let $q \geq 7/2$ and $\lambda \in \mathbb{R}$. Let $(X,\psi), (X',\psi')$ be two solutions of (4.1) in the space*

$$C^0\big([0,\tau]; H^2\big(\mathbb{R}^3;\mathbb{C}^{N_{\mathrm{el}}}\big)\big) \cap C^1\big([0,\tau]; L^2\big(\mathbb{R}^3;\mathbb{C}^{N_{\mathrm{el}}}\big)\big) \times C^2\big([0,\tau];\mathbb{R}^{3N_{\mathrm{nuc}}}\big)$$

*for some $\tau > 0$. Then, we have for all $t \in [0, \tau]$*

$$\big|\big(\ddot{X} - \ddot{X}'\big)(t)\big| \leq C[|(X - X')(t)| + \|(\psi - \psi')(t)\|_{L^{3,\infty}}], \tag{4.122}$$

$$\|(\psi - \psi')(t)\|_{L^{3,\infty}} \leq$$
$$\leq C \int_0^t \frac{1}{\sqrt{t-\sigma}}[|(X - X')(\sigma)| + \|(\psi - \psi')(\sigma)\|_{L^{3,\infty}}]\mathrm{d}\sigma, \tag{4.123}$$

*where* $C = C\big(\|\psi\|_{C^0([0,\tau];H^2)}, \|\psi'\|_{C^0([0,\tau];H^2)}\big)$.

Here, $L^{3,\infty}$ indicates a weak Lebesgue space: see also Section A.2.

*Proof of* (4.122). In this proof, we use for shorthand notation the function $\Xi : \mathbb{R}^3 \longrightarrow \mathbb{R}^3$ (a.e.), $x \longmapsto x|x|^{-3}$.

We have for all $t \in [0, \tau]$ and $K \in \{1, \dots, N_{\mathrm{nuc}}\}$

$$\begin{aligned}
&\big|\big(\ddot{X}_K - \ddot{X}'_K\big)(t)\big| \leq \\
&\leq |A^1_K[\rho(t)](X(t)) - A^1_K[\rho'(t)](X'(t))| + |A^2_K(X(t)) - A^2_K(X'(t))| \\
&\leq \underbrace{|A^1_K[\rho(t)](X(t)) - A^1_K[\rho(t)](X'(t))|}_{=:(\mathrm{I})} \\
&+ \underbrace{|A^1_K[\rho(t)](X'(t)) - A^1_K[\rho'(t)](X'(t))|}_{=:(\mathrm{II})} + \underbrace{|A^2_K(X(t)) - A^2_K(X'(t))|}_{=:(\mathrm{III})}.
\end{aligned}$$

By Lemma 4.11 on the force functions, $A^1_K[\rho]$ are uniformly Lipschitz continuous in the nuclear variable for all $t \in [0, \tau]$ and $k$, by which

$$\begin{aligned}
(\mathrm{I}) &\lesssim \sum_{k=1}^{N_{\mathrm{el}}} |(\psi_k(t), \Xi(\cdot - X_K(t))\psi_k(t))_{L^2} - (\psi_k(t), \Xi(\cdot - X'_K(t))\psi_k(t))_{L^2}| \\
&\overset{(4.29)}{\leq} C_{\mathrm{I}}|(X_K - X'_K)(t)| \leq C_{\mathrm{I}}|(X - X')(t)|
\end{aligned}$$

for some $C_{\mathrm{I}} = C_{\mathrm{I}}(\|\psi\|_{C^0([0,\tau];H^2)}) > 0$. Also,

$$
\begin{aligned}
&(\mathrm{II}) \lesssim \\
&\lesssim \sum_{k=1}^{N_{\mathrm{el}}} |(\psi_k(t), \Xi(\cdot - X_K(t))(\psi_k - \psi_k')(t))_{L^2} \\
&\quad + ((\psi_k - \psi_k')(t), \Xi(\cdot - X_K'(t))\psi_k'(t))_{L^2}| \\
&\lesssim \sum_{k=1}^{N_{\mathrm{el}}} [|(|\cdot - X_K(t)|^{-1}\psi_k(t), |\cdot - X_K(t)|^{-1}(\psi_k - \psi_k')(t))_{L^2}| \\
&\quad + \big|\big(|\cdot - X_K'(t)|^{-1}(\psi_k - \psi_k')(t), |\cdot - X_K'(t)|^{-1}\psi_k'(t)\big)_{L^2}\big|] \qquad (4.124) \\
&\lesssim \sum_{k=1}^{N_{\mathrm{el}}} \big[\big\||\cdot - X_K(t)|^{-1}\psi_k(t)\big\|_{L^2}\big\||\cdot - X_K(t)|^{-1}(\psi_k - \psi_k')(t)\big\|_{L^2} \\
&\quad + \big\||\cdot - X_K'(t)|^{-1}\psi_k'(t)\big\|_{L^2}\big\||\cdot - X_K'(t)|^{-1}(\psi_k - \psi_k')(t)\big\|_{L^2}\big] \qquad (4.125) \\
&\lesssim \sum_{k=1}^{N_{\mathrm{el}}} [\|\nabla_x \psi_k(t)\|_{L^2} + \|\nabla_x \psi_k'(t)\|_{L^2}]\big\|\big[|\cdot|^{-2} * |\psi_k - \psi_k'|^2(t,\cdot)\big]\big\|_{L^\infty}^{1/2} \\
&\qquad\qquad (4.126) \\
&\lesssim \big\||\cdot|^{-2}\big\|_{L^{3/2,\infty}}^{1/2} \sum_{k=1}^{N_{\mathrm{el}}} (\|\psi_k(\sigma)\|_{H^2} + \|\psi_k'(\sigma)\|_{H^2}) \sum_{\ell=1}^{N_{\mathrm{el}}} \big\||\psi_\ell - \psi_\ell'|^2(t)\big\|_{L^{3/2,\infty}}^{1/2} \\
&\qquad\qquad (4.127) \\
&\le C_{\mathrm{II}} \|(\psi - \psi')(t)\|_{L^{3,\infty}} \qquad (4.128)
\end{aligned}
$$

for some $C_{\mathrm{II}} = C_{\mathrm{II}}\big(\|\psi\|_{C^0([0,\tau];H^2)}, \|\psi'\|_{C^0([0,\tau];H^2)}\big) > 0$. Here, we used that $|\Xi| = |\cdot|^{-2}$ in (4.124), the Cauchy–Schwarz and Hardy's inequalities (A.4) in (4.125,4.126), (A.13) in (4.127), and (A.12) and $'\big\|\phi^2\big\|_{L^{3/2,\infty}} = \|\phi\|_{L^{3,\infty}}^2$ (since $\big(\phi^2\big)^* = \big(\phi^*\big)^2$) in (4.128). Since $X, X' \in \mathcal{B}_{\mathrm{nuc}}(\tau)$, we can bound (III) similarly to part 1 of the proof of Lemma 4.20:

$$
\begin{aligned}
(\mathrm{III}) &\lesssim \sum_{\substack{L=1,\\ L\neq K}}^{N_{\mathrm{nuc}}} |\Xi((X_K - X_{1L})(t)) - \Xi((X_K' - X_{2L})(t))| \\
&\lesssim_{\delta, X^0} |(X - X')(t)|.
\end{aligned}
$$

Since these results hold for all $k$, (4.122) follows.

*Proof of* (4.123).

Similarly to the proof of Lemma 4.21,

$$\begin{cases} i\dfrac{\partial}{\partial t}(\psi - \psi') = -\frac{1}{2}\Delta(\psi - \psi') + V_{\text{ext}}[X](\psi - \psi') \\ \qquad\qquad\qquad + \mathcal{V}_{\text{HX}}[\rho](\psi - \psi') + \widetilde{\zeta}, \\ (\psi - \psi')(0) = 0, \end{cases}$$

where $\widetilde{\zeta} := \widetilde{\zeta}^1 + \widetilde{\zeta}^2 + \widetilde{\zeta}^3$, with for $j \in \{1,2,3\}$, $\widetilde{\zeta}^j$ being $\zeta_n^j$ with $(X_n, \psi_n) \longmapsto (X', \psi')$. As the operator $-\Delta/2$ generates the free propagator, we write the equivalent integral equation for all $t \in [0, \tau]$

$$(\psi - \psi')(t) = -i \int_0^t U_0(t-\sigma) \Big\{ V_{\text{ext}}[X(\sigma)](\psi - \psi')(\sigma) + \mathcal{V}_{\text{HX}}[\rho](\psi - \psi')(\sigma) + \widetilde{\zeta}(\sigma) \Big\} \mathrm{d}\sigma.$$

In [CB99, Lemma 6], the following result on the free propagator is proven: for all $\sigma \in (0, \tau]$ and $f \in L^{3/2,\infty}$, we have

$$\|U_0(\sigma) f\|_{L^{3,\infty}} \lesssim \frac{1}{\sqrt{\sigma}} \|f\|_{L^{3/2,\infty}}.$$

Using this result and the quasi-triangle inequality (A.2), we get for all $t \in [0, \tau]$ and $k$

$$\begin{aligned} &\|(\psi_k - \psi_k')(t)\|_{L^{3,\infty}} \lesssim \\ &\lesssim \int_0^t \frac{1}{\sqrt{t-\sigma}} \big[ \|(V_{\text{ext}}[X(\sigma)](\psi - \psi'))_k(\sigma)\|_{L^{3/2,\infty}} \\ &\quad + \|(\mathcal{V}_{\text{H}}[\rho](\psi - \psi'))_k(\sigma)\|_{L^{3/2,\infty}} + \|(\mathcal{V}_{\text{x}}[\rho](\psi - \psi'))_k(\sigma)\|_{L^{3/2,\infty}} \\ &\quad + \sum_{j \in \{1,2,3\}} \big\| \big(\widetilde{\zeta}^j(\sigma)\big)_k \big\|_{L^{3/2,\infty}} \big] \mathrm{d}\sigma. \end{aligned}$$

Since $\|\cdot\|_{\mathbb{R}^3}^{-1} \in L^{3,\infty}$ by (A.12), we arrive at the following estimates for all $\sigma \in (0, t)$ and $k$. Using the quasi-triangle inequality (A.2) and Hölder's inequality (A.11) on $L^{3/2,\infty}$, we have

$$\begin{aligned} &\|(V_{\text{ext}}[X(\sigma)](\psi - \psi'))_k(\sigma)\|_{L^{3/2,\infty}} \lesssim \\ &\lesssim \sum_{L=1}^{N_{\text{nuc}}} \big\| |\cdot - X_L(\sigma)|^{-1} \big\|_{L^{3,\infty}} \|(\psi_k - \psi_k')(\sigma)\|_{L^{3,\infty}} \\ &\lesssim \big\| |\cdot|^{-1} \big\|_{L^{3,\infty}} \|(\psi_k - \psi_k')(\sigma)\|_{L^{3,\infty}} \lesssim \|(\psi_k - \psi_k')(\sigma)\|_{L^{3,\infty}}. \end{aligned}$$

We also get

$$\|(\mathcal{V}_{\mathrm{H}}[\rho](\psi-\psi'))_k(\sigma)\|_{L^{3/2,\infty}} \lesssim \|\rho(\sigma,\cdot) * |\cdot|^{-1}\|_{L^{3,\infty}} \|(\psi_k-\psi_k')(\sigma)\|_{L^{3,\infty}} \tag{4.129}$$

$$\lesssim \|\rho(\sigma)\|_{L^1} \big\||\cdot|^{-1}\big\|_{L^{3,\infty}} \|(\psi_k-\psi_k')(\sigma)\|_{L^{3,\infty}} \leq C_{\mathrm{H}} \|(\psi_k-\psi_k')(\sigma)\|_{L^{3,\infty}} \tag{4.130}$$

for some $C_{\mathrm{H}} = C_{\mathrm{H}}(\|\psi\|_{C^0([0,\tau];H^2)}) > 0$. Here, we used Hölder's inequality (A.11) on $L^{3/2,\infty}$ in (4.129) and Young's convolution inequality (A.10) on $L^{3,\infty}$ in (4.130). Furthermore, we have

$$\|(\mathcal{V}_{\mathrm{x}}[\rho][\psi-\psi'])_k(\sigma)\|_{L^{3/2,\infty}} \lesssim_\lambda \big\|[\rho(\sigma)]^{q-1}\big\|_{L^{3,\infty}} \|(\psi_k-\psi_k')(\sigma)\|_{L^{3,\infty}} \tag{4.131}$$

$$\lesssim \big\|[\rho(\sigma)]^{q-1}\big\|_{L^3} \|(\psi_k-\psi_k')(\sigma)\|_{L^{3,\infty}} \leq C_{\mathrm{x}} \|(\psi_k-\psi_k')(\sigma)\|_{L^{3,\infty}} \tag{4.132}$$

for some $C_{\mathrm{x}} = C_{\mathrm{x}}(\|\psi\|_{C^0([0,\tau];H^2)}, q) > 0$. Here, we used Hölder's inequality (A.11) on $L^{3/2,\infty}$ in (4.131). In (4.132), we first used [BS88, Chapter 4, Prop. 4.2.], and then the quasi-triangle inequality (A.2), Sobolev's inequality with interpolation in Corollary A.8, and the embedding of $H^2$ into $L^\infty$, by which, with $\theta := 6(q-1) > 6$, we have

$$\big\|[\rho(\sigma)]^{q-1}\big\|_{L^3}^3 \lesssim_q \sum_{k=1}^{N_{\mathrm{el}}} \big\|[\psi_k(\sigma)]^{(\theta-6)+6}\big\|_{L^1} \lesssim \sum_{k=1}^{N_{\mathrm{el}}} \|\psi_k(\sigma)\|_{L^\infty}^{\theta-6} \|\psi_k(\sigma)\|_{L^6}^6$$
$$\lesssim \sum_{k=1}^{N_{\mathrm{el}}} \|\psi_k\|_{C^0([0,\tau];H^2)}^{\theta}.$$

We also have

$$\begin{aligned}
&\big\|\big(\widetilde{\zeta}^1(\sigma)\big)_k\big\|_{L^{3/2,\infty}} \lesssim \\
&\lesssim \sum_{L=1}^{N_{\mathrm{nuc}}} \big\|\big(|\cdot - X_L(\sigma)|^{-1} - |\cdot - X_L'(\sigma)|^{-1}\big)\psi_k'(\sigma,\cdot)\big\|_{L^{3/2,\infty}} && (4.133)\\
&= \sum_{L=1}^{N_{\mathrm{nuc}}} \big\|\big(|\cdot - (X_L - X_L')(\sigma)|^{-1} - |\cdot|^{-1}\big)\psi_k'(\sigma,\cdot + X_L')\big\|_{L^{3/2,\infty}} && (4.134)\\
&\lesssim \|\psi_k'(\sigma)\|_{L^\infty} \sum_{L=1}^{N_{\mathrm{nuc}}} \big\||\cdot|^{-1}|\cdot - (X_L - X_L')(\sigma)|^{-1}\big\|_{L^{3/2,\infty}} |(X_L - X_L')(\sigma)| && (4.135)\\
&\lesssim \|\psi_k'\|_{C^0([0,\tau];H^2)} \big\||\cdot|^{-1}\big\|_{L^{3,\infty}} \sum_{L=1}^{N_{\mathrm{nuc}}} \big\||\cdot - (X_L - X_L')(\sigma)|^{-1}\big\|_{L^{3,\infty}} \times \\
&\qquad \times |(X_L - X_L')(\sigma)| && (4.136)\\
&\lesssim_{N_{\mathrm{nuc}}} \|\psi_k'\|_{C^0([0,\tau];H^2)} \big\||\cdot|^{-1}\big\|_{L^{3,\infty}}^2 |(X - X')(\sigma)| && (4.137)\\
&\lesssim \|\psi_k'\|_{C^0([0,\tau];H^2)} |(X - X')(\sigma)|.
\end{aligned}$$

where we used the quasi-triangle inequality (A.2) in (4.133), shift invariance of the weak Lebesgue norms in (4.134,4.137), the reverse triangle inequality $||\cdot| - |\cdot - (X_L - X_L')(\sigma)|| \leq |(X_L - X_L')(\sigma)|$ in (4.135) and Hölder's inequality (A.11) on $L^{3/2,\infty}$ and the embedding of $H^2$ into $L^\infty$ in (4.136). In addition, we have

$$\begin{aligned}
&\big\|(\widetilde{\zeta}^2(\sigma))_k\big\|_{L^{3/2,\infty}} \lesssim \\
&\lesssim \sum_{\ell=1}^{N_{\mathrm{el}}} \big\|\big\{\big[\overline{(\psi_\ell - \psi_\ell')(\sigma)}(\psi_\ell + \psi_\ell')(\sigma)\big] * |\cdot|^{-1}\big\}\psi_k'(\sigma)\big\|_{L^{3/2,\infty}} && (4.138)\\
&\lesssim \sum_{\ell=1}^{N_{\mathrm{el}}} \big\|[\overline{(\psi_\ell - \psi_\ell')(\sigma)}(\psi_\ell + \psi_\ell')(\sigma)] * |\cdot|^{-1}\big\|_{L^{6,\infty}} \|\psi_k'(\sigma)\|_{L^{2,\infty}} && (4.139)\\
&\lesssim \sum_{\ell=1}^{N_{\mathrm{el}}} \big\|\big[\overline{(\psi_\ell - \psi_\ell')(\sigma)}(\psi_\ell + \psi_\ell')(\sigma)\big] * |\cdot|^{-1}\big\|_{L^{6,2}} \|\psi_k'(\sigma)\|_{L^2} && (4.140)\\
&\lesssim \|\psi_k'\|_{C^0([0,\tau];H^2)} \sum_{\ell=1}^{N_{\mathrm{el}}} \big\|\overline{(\psi_\ell - \psi_\ell')(\sigma)}(\psi_\ell + \psi_\ell')(\sigma)\big\|_{L^{6/5,2}} \big\||\cdot|^{-1}\big\|_{L^{3,\infty}} && (4.141)
\end{aligned}$$

$$\lesssim \|\psi_k'\|_{C^0([0,\tau];H^2)} \sum_{\ell=1}^{N_{\mathrm{el}}} [\|\psi_\ell(\sigma)\|_{L^2} + \|\psi_\ell'(\sigma)\|_{L^2}] \|(\psi_\ell - \psi_\ell')(\sigma)\|_{L^{3,\infty}} \tag{4.142}$$

$$\leq C_2 \|(\psi - \psi')(\sigma)\|_{L^{3,\infty}} \tag{4.143}$$

for some $C_2 = C_2(\|\psi\|_{C^0([0,\tau];H^2)}, \|\psi'\|_{C^0([0,\tau];H^2)}) > 0$. Here, we used the quasi-triangle inequality (A.2) in (4.138), Hölder's inequality (A.11) on $L^{3/2,\infty}$ in (4.139), [BS88, Chapter 4, Prop. 4.2.] in (4.140), Young's convolution inequality (A.10) on $L^{6,2}$ in (4.141), and Hölder's inequality (A.11) on $L^{6/5,2}$ in (4.142). Additionally, we have

$$\begin{aligned}
&\big\| \big(\widetilde{\zeta}^3(\sigma)\big)_k \big\|_{L^{3/2,\infty}} \overset{(4.74)}{\lesssim}_{\lambda,q} \\
&\lesssim_{\lambda,q} \big\| [\rho(\sigma)]^{q-3/2} + [\rho'(\sigma)]^{q-3/2} \big\|_{L^\infty} \|\psi_k'(\sigma)|\psi(\sigma) - \psi'(\sigma)|\|_{L^{3/2,\infty}} \\
&\lesssim \big[ \|\rho(\sigma)\|_{L^\infty}^{q-3/2} + \|\rho'(\sigma)\|_{L^\infty}^{q-3/2} \big] \|\psi_k'(\sigma)\|_{L^{3,\infty}} \||(\psi - \psi')(\sigma)|\|_{L^{3,\infty}}
\end{aligned} \tag{4.144}$$

$$\begin{aligned}
\lesssim_q &\Big[ \sum_{\ell'=1}^{N_{\mathrm{el}}} \|\psi_{\ell'}(\sigma)\|_{H^2}^{2q-3} + \sum_{k'=1}^{N_{\mathrm{el}}} \|\psi_{k'}'(\sigma)\|_{H^2}^{2q-3} \Big] \|\psi_k'(\sigma)\|_{L^3} \times \\
&\times \sum_{\ell=1}^{N_{\mathrm{el}}} \|(\psi_\ell - \psi_\ell')(\sigma)\|_{L^{3,\infty}} \leq C_3 \|(\psi - \psi')(\sigma)\|_{L^{3,\infty}}.
\end{aligned} \tag{4.145}$$

for some $C_3 = C_3(\|\psi\|_{C^0([0,\tau];H^2)}, \|\psi'\|_{C^0([0,\tau];H^2)}, q) > 0$. Here, we used Hölder's inequality (A.11) on $L^{3/2,\infty}$ in (4.144). In (4.145), we first use (4.80), [BS88, Chapter 4, Prop. 4.2.] and the quasi-triangle inequality, and then Sobolev's embedding theorem with interpolation in Corollary A.8. Since all of these estimates hold for all $\sigma \in (0,t)$, and $j$, (4.123) follows. □

*Proof of Theorem 4.1.* Let $\tau > 0$ be such that the following statements hold. For given $\psi \in \mathcal{B}_{\mathrm{el}}(\tau)$, (4.92) has a unique solution $X \in \mathcal{B}_{\mathrm{nuc}}(\tau) \cap C^2\big([0,\tau]; B_\delta\big(X^0\big)\big)$, and for given $X \in \mathcal{B}_{\mathrm{nuc}}(\tau)$, (4.107) has a unique solution $\psi \in \mathcal{B}_{\mathrm{el}}(\tau)$. Existence of such $\tau$ has been proven in Lemmas 4.20 and 4.21. Existence of the solution $(X,\psi)$ of (4.1) in the space

$$C^0\big([0,\tau]; H^2\big(\mathbb{R}^3; \mathbb{C}^{N_{\mathrm{el}}}\big)\big) \cap C^1\big([0,\tau]; L^2\big(\mathbb{R}^3; \mathbb{C}^{N_{\mathrm{el}}}\big)\big) \times C^2\big([0,\tau]; \mathbb{R}^{3N_{\mathrm{nuc}}}\big)$$

has been proven in Lemma 4.23. Uniqueness of this solution follows from Lemma 4.24. For two solutions $(X,\psi), (X',\psi')$ in this space and $p > 2$,

let us define the function $h \in C^0([0,\tau])$ by

$$h(t) := [|(X - X')(t)| + \|(\psi - \psi')(t)\|_{L^{3,\infty}}]^p.$$

Since $X$ and $X'$ both solve (4.92) on $[0,\tau]$ and thus are fixed points of the mapping $\mathcal{T}$ in (4.100), for all $t \in [0,\tau]$

$$\begin{aligned} |(X - X')(t)| &\leq \Big| \int_0^t (t-\sigma)\big(\ddot{X} - \ddot{X}'\big)(\sigma) \mathrm{d}\sigma \Big| \\ &\leq \int_0^t (t-\sigma) \big|\big(\ddot{X} - \ddot{X}'\big)(\sigma)\big| \mathrm{d}\sigma. \end{aligned}$$

Now, using this in combination with Lemma 4.24 in (4.146) and Hölder's inequality combined with the fact that since $p > 2$, its Hölder conjugate $p' < 2$, which ensures that the $L^{p'}([0,t])$ norm of $t - \cdot + (t-\cdot)^{-1/2}$ is finite in (4.147), for all $t \in [0,\tau]$

$$\begin{aligned} &h(t) \lesssim_p \\ &\lesssim_p C \bigg\{ \int_0^t \bigg( t - \sigma + \frac{1}{\sqrt{t-\sigma}} \bigg) [|(X - X')(\sigma)| + \|(\psi - \psi')(\sigma)\|_{L^{3,\infty}}] \mathrm{d}\sigma \bigg\}^p \qquad (4.146) \\ &\lesssim C \bigg\| \bigg( t - \cdot + \frac{1}{\sqrt{t-\cdot}} \bigg) h^{1/p} \bigg\|_{L^1([0,t])}^p \\ &\lesssim C \bigg\| t - \cdot + \frac{1}{\sqrt{t-\cdot}} \bigg\|_{L^{p'}([0,t];\mathbb{R})}^p \big\| h^{1/p} \big\|_{L^p([0,t])}^p \lesssim_\tau C \int_0^t h(\sigma) \mathrm{d}\sigma, \qquad (4.147) \end{aligned}$$

where $C = C\big(\|\psi\|_{C^0([0,\tau];H^2)}, \|\psi'\|_{C^0([0,\tau];H^2)}\big)$ is from Lemma 4.24. Now, using Grönwall's inequality (A.15), we obtain $h \leq 0$ on $[0,\tau]$. Since $h \geq 0$ too by definition, and $h(0) = 0$ since $X(0) = X'(0) = X^0$ and $\psi(0) = \psi'(0) = \psi^0$, we get $h \equiv 0$, by which $(X,\psi) = (X',\psi')$. This completes the proof. □

# Chapter 5

# Towards existence of weak solutions for $1 < q \leq 5/3$ and $\lambda < 0$

In this chapter, we show, under a conjecture on convergence, results towards global-in-time existence of solutions to a weak formulation of the original system

$$i\dot{\psi}_k = -\tfrac{1}{2}\Delta_x\psi_k - \sum_{K=1}^{N_{\mathrm{nuc}}} \frac{Z_K}{|\cdot - X_K|}\psi_k + \left(\frac{1}{|\cdot|} * \rho\right)\psi_k + \lambda\rho^{q-1}\psi_k, \quad (5.1a)$$

$$\ddot{X}_K = \frac{Z_K}{M_K}\left[\int \frac{x - X_K}{|x - X_K|^3}\rho(x)\mathrm{d}x + \sum_{L=1, L\neq K}^{N_{\mathrm{nuc}}} Z_L \frac{X_K - X_L}{|X_K - X_L|^3}\right]. \quad (5.1b)$$

in the setting of the Sobolev space $H^1$ for the Kohn–Sham wave functions $\psi_k$. We obtain this result in the range of exponents $1 < q \leq 5/3$ in the pure-power exchange term within the generalisation of the local density approximation, which includes the physically relevant value $q = 4/3$, and for the case of a negative sign for $\lambda = -|\lambda|$, which also corresponds to the value in the original formulation of the local density approximation (3.1).

In Section 5.1.2, we derive estimates for several terms in the total energy. Eventually, we bound the $H^1$ norm of the Kohn–Sham wave functions $\psi_k$ by an expression involving the total energy and the electronic charge.

In Section 5.2, we apply a Galerkin-type method, based on the variational formulation discussed in Section 3.3. We prove existence of solu-

tions $\big(\psi^n, X^n\big)$ in the space $C^1\big([0,T];H^1\big) \times C^2\big([0,T];\mathbb{R}^{3N_{\mathrm{nuc}}}\big)$ for arbitrary $T > 0$ to the truncated system of order $n \in \mathbb{N}$

$$\big(i\dot{\psi}_k^n(t), \phi^\nu\big)_{L^2} = \tfrac{1}{2}\big(\nabla_x \psi_k^n(t), \nabla_x \phi^\nu\big)_{L^2} +$$
$$\Big( -\sum_{K=1}^{N_{\mathrm{nuc}}} \frac{Z_K}{|x - X_K^n|}\psi_k^n(t) + \int \frac{\rho^n(t,x')}{|\cdot - x'|}\mathrm{d}x'\psi_k^n(t) - |\lambda|\big[\rho^n(t)\big]^{q-1}\psi_k^n(t), \phi^\nu\Big)_{L^2},$$
$$\ddot{X}_K^n(t)\cdot Y = Z_K \int \rho(t,x)\frac{\big(x - X_K^n(t)\big)}{\big|x - X_K^n(t)\big|^3}\mathrm{d}x \cdot Y$$
$$+ \sum_{L\neq K}^{N_{\mathrm{nuc}}} Z_K Z_L \frac{X_K^n(t) - X_L^n(t)}{\big|X_K^n(t) - X_L^n(t)\big|^3}\cdot Y,$$
$$\psi^n(0) = \psi^{n0} = \sum_{\nu=1}^{n} a_{k,\nu}^0 \phi^\nu \in W, \quad \big(X^n(0), \dot{X}^n(0)\big) = \big(X^0, V^0\big) \in \mathbb{R}^{6N_{\mathrm{nuc}}}.$$

Here, $Y \in \mathbb{R}^3$, and the approximated solutions $\psi^n$ of order $n \in \mathbb{N}$ are of the form

$$\psi_k^n(t) = \sum_{\nu=1}^{n} a_{k,\nu}^n(t)\phi^\nu \in \mathrm{span}\big\{\phi^\nu\big\}_{\nu=1}^n \subset W,$$

with $a_{k,\nu}^n$ time-dependent scalar coefficients of class $C^1$ in $\mathbb{C}$ and $\phi^\nu$ the (orthonormal) eigenvectors of the eigenvalue problem $-\Delta_x\phi + |x|^2\phi = E\phi$ on $x \in \mathbb{R}^3$, which form a basis of the Hilbert space

$$W := \Big\{\phi \in H^1\big(\mathbb{R}^3\big)\Big| \int |x|^2|\phi(x)|^2\mathrm{d}x < \infty\Big\}.$$

For these approximate solutions, we also prove conservation of total energy and charge.

In Section 5.3, we perform a convergence argument in the limit $n \longrightarrow \infty$, using the following conjecture.

**Conjecture 5.1.** *Let $T > 0$ be arbitrary, and let $\big\{\psi^n, X^n\big\}_{n\in\mathbb{N}}$ denote a sequence of solutions of (5.19). Then, for all $K = 1, \ldots, N_{\mathrm{nuc}}$*

$$\int_0^T \int \frac{1}{|x - X_K^n(t)|^2}\big[|\psi^n(t,x)|^2 - |\psi(t,x)|^2\big]\mathrm{d}x\mathrm{d}t \xrightarrow{n\longrightarrow\infty} 0.$$

Using this conjecture, we arrive at the following existence result on weak solutions. Here, $L^2L^2 = L^2\big((0,T);L^2(\mathbb{R}^3;\mathbb{C}^{N_{\mathrm{el}}})\big)$ and $L^\infty H^1 = L^\infty\big((0,T);H^1(\mathbb{R}^3;\mathbb{C}^{N_{\mathrm{el}}})\big)$; see also Appendix A.2.

**Theorem 5.2.** *Let $1 < q \leq 5/3$ and $\lambda < 0$. Further, let $\psi^0 \in W, X^0 \in \mathbb{R}^{3N_{\mathrm{nuc}}}, V^0 \in \mathbb{R}^{3N_{\mathrm{nuc}}}$ such that $X_K^0 \neq X_L^0$ for $1 \leq K \neq L \leq N_{\mathrm{nuc}}$. Let $T > 0$ be arbitrary. Then, there exists a pair*

$$(\psi, X) \in L^2\big([0,T]; W^{N_{\mathrm{el}}}\big) \cap L^\infty\big((0,T); H^1(\mathbb{R}^3; \mathbb{C}^{N_{\mathrm{el}}})\big) \times C^0\big([0,T]; \mathbb{R}^{3N_{\mathrm{nuc}}}\big)$$

*which solves (5.1) in the sense that for all*

$$\begin{aligned} &v \in L^2\big([0,T]; H^1(\mathbb{R}^3)\big) \cap H^1\big([0,T]; L^2(\mathbb{R}^3)\big), \\ &Y \in C_{\mathrm{c}}^2\big((0,T); \mathbb{R}^3\big), \end{aligned}$$

*$(\psi, X)$ is a solution of the initial-value problem*

$$\begin{aligned} -\big(i\psi_k, \dot{v}\big)_{L^2L^2} = \tfrac{1}{2}(\nabla_x \psi_k, \nabla_x v)_{L^2L^2} + \Big( &- \sum_{K=1}^{N_{\mathrm{nuc}}} \frac{Z_K}{|x - X_K|}\psi_k \\ &+ \int \frac{\rho(x')}{|\cdot - x'|}\mathrm{d}x'\psi_k - |\lambda|\rho^{q-1}\psi_k, v\Big)_{L^2L^2}, \end{aligned} \tag{5.3a}$$

$$\begin{aligned} \int_0^T X_K(t) \cdot \ddot{Y}(t)\mathrm{d}t = \int_0^T Z_K \int \rho(t,x)\frac{x - X_K(t)}{|x - X_K(t)|^3}\mathrm{d}x \cdot Y(t)\mathrm{d}t \\ + \int_0^T \sum_{L \neq K}^{N_{\mathrm{nuc}}} Z_K Z_L \frac{X_K(t) - X_L(t)}{|X_K(t) - X_L(t)|^3} \cdot Y(t)\mathrm{d}t, \end{aligned} \tag{5.3b}$$

$$\psi(0) = \psi^0, X(0) = X^0, \dot{X}(0) = V^0. \tag{5.3c}$$

The proof of the above result combines estimates on terms in the total energy with (mainly compactness) properties of $W$ and the approximated solutions to the truncated system.

See Appendix A for the definitions of the notation we use.

## 5.1 Preliminary results

### 5.1.1 Notes on the Poisson equation

The material in this section is adapted from [Mer22]. Note that the results in this section are formulated for real-valued functions, but can easily be generalised to complex-valued ones.

**Proposition 5.3.** *Let $u \in L^2_{\mathrm{loc}}(\mathbb{R}^N)$, $N \geq 3$, such that*

$$\iint \frac{[u(x)]^2[u(x')]^2}{|x - x'|^{N-2}}\mathrm{d}x\mathrm{d}x' < \infty.$$

*Then,*

$$\phi_u := \frac{1}{\omega|x|^{N-2}} * u^2$$

*is the unique weak solution to* $-\Delta_x \phi = u^2$ *in* $D^{1,2}\big(\mathbb{R}^N\big)$. *Moreover, it holds that*

$$\|\phi_u\|^2_{D^{1,2}(\mathbb{R}^N)} = \int \phi_u(x)[u(x)]^2 \mathrm{d}x = \iint \frac{[u(x)]^2[u(x')]^2}{\omega|x-x'|^{N-2}} \mathrm{d}x\mathrm{d}x'.$$

*Here,* $\omega = (N-2)\mu\big(\mathbb{S}^{N-1}\big)$, *with* $\mu\big(\mathbb{S}^{N-1}\big)$ *denoting the volume of the unit sphere* $\mathbb{S}^{N-1}$ *in* $\mathbb{R}^N$.

*Proof.* For simplicity, we consider $N = 3$, with $\omega = 4\pi$. First, we show uniqueness of a possible solution. Suppose there are two solutions $\phi_1, \phi_2$: then,

$$\begin{cases} -\Delta_x \phi_1 = u^2 \\ -\Delta_x \phi_2 = u^2 \end{cases} \quad \text{in } D^{1,2}(\mathbb{R}^3).$$

Subtracting the two solutions, we obtain

$$\int |\nabla_x(\phi_1 - \phi_2)(x)|^2 \mathrm{d}x = 0.$$

Hence, by Sobolev's inequality, $\phi_1 \equiv \phi_2$.
Also, we observe that the identity

$$\|\phi_u\|^2_{D^{1,2}} = \int \phi_u(x)[u(x)]^2 \mathrm{d}x = \iint \frac{[u(x)]^2[u(x')]^2}{\omega|x-x'|} \mathrm{d}x\mathrm{d}x'$$

easily follows testing $-\Delta_x \phi_u = u^2$ with $\phi_u$.

We are left to show that $\phi_u \in D^{1,2}(\mathbb{R}^3)$, and that $\int \nabla_x \phi_u \nabla_x \xi = \int u^2 \xi$ for all $\xi \in D^{1,2}$. We break the proof into several steps.

*Step 1.*
Set

$$f_n := \min\{u, n\}\chi_{\{|x|<n\}}.$$

We note the following:

1. $f_n$ has compact support,
2. $f_n$ is non-decreasing,

3. $f_n \nearrow u$ almost everywhere,

4. $f_n \in L^\infty(\mathbb{R}^3)$.

We then claim that

$$\phi_n(x) := \int \frac{[f_n(x')]^2}{4\pi|x-x'|}\mathrm{d}x'$$

is such that

$$-\int \phi_n(x)\Delta_x\xi(x)\mathrm{d}x = \int [f_n(x)]^2\xi(x)\mathrm{d}x \tag{5.4}$$

for all $\xi \in C_c^\infty$. Moreover $\phi_n \in C^1$ and $\|\phi_n\|_{D^{1,2}} < C$ for all $n$.

In fact, (5.4) follows by [LL01, Theorem 6.21], from which for all $j = 1, 2, 3$

$$\partial_j\phi_n(x) = \int \partial_j G_{x'}(x)[f_n(x')]^2\mathrm{d}x',$$

where for all $j = 1, 2, 3$

$$G_{x'}(x) := \frac{1}{4\pi|x-x'|}, \qquad \partial_j G_{x'}(x) = -\frac{1}{4\pi}\frac{x-x'}{|x-x'|^3},$$

and

$$\int G_{x'}(x)\Delta_x\xi(x)\mathrm{d}x = -\xi(x)$$

for all $\xi \in C_c^\infty$. By property 4. of $f_n$ and [LL01, Theorem 10.2], $\phi_n \in C^1$. Moreover,

$$\begin{aligned}
\int |\nabla_x\phi_n(x)|^2\mathrm{d}x &= \sum_{j=1}^3 \int |\partial_j\phi_n(x'')|^2\mathrm{d}x'' \\
&= \sum_{j=1}^3 \int \left[\int \frac{1}{4\pi}\frac{x_j''-x_j'}{|x''-x'|^3}[f_n(x')]^2\mathrm{d}x'\right]\left[\int \frac{1}{4\pi}\frac{x_j''-x_j}{|x''-x|^3}[f_n(x)]^2\mathrm{d}x\right]\mathrm{d}x'' \\
&\leq 3\int [f_n(x)]^2 \int [f_n(x')]^2 \int \frac{1}{|x''-x'|^2}\frac{1}{|x''-x|^2}\mathrm{d}x''\mathrm{d}x'\mathrm{d}x.
\end{aligned}$$

Using the substitution $\omega = x'' - x'$, the last integral in the expression above becomes

$$\int \frac{1}{|\omega|^2}\frac{1}{|\omega-(x-x')|^2}\mathrm{d}\omega.$$

By [Lan72, p.45], it follows that

$$\int \frac{1}{|\omega|^2} \cdot \frac{1}{|\omega - (x - x')|^2} \mathrm{d}\omega = \frac{C}{|x - x'|}$$

for some constant $C > 0$. Hence,

$$\int |\nabla_x \phi_n(x)|^2 \mathrm{d}x \lesssim \iint \frac{[u(x)]^2 [u(x')]^2}{|x - x'|} \mathrm{d}x \mathrm{d}x'$$

is the claimed uniform bound.

*Step 2.*
Since $\{\phi_n\}_{n \in \mathbb{N}} \subset D^{1,2}$ is uniformly bounded in $D^{1,2}$, $\phi_n \rightharpoonup \phi \in D^{1,2}$ by Banach–Alaoglu.
We claim that

$$\phi = \phi_u = \frac{1}{4\pi |\cdot|} * u^2.$$

Indeed, by [LL01, Theorem 8.6], $\phi_n \longrightarrow \phi$ in $L^p_{\mathrm{loc}}$, $p < 6$ and a.e. Hence, by monotone convergence,

$$\phi_n = \int \frac{[f_n(x')]^2}{4\pi |\cdot - x'|} \mathrm{d}x' \longrightarrow \phi_u$$

almost everywhere, and we can conclude our claim by uniqueness of the limit.

Roughly speaking, the sequence $\{\phi_n\}_{n \in \mathbb{N}}$ approximates $\phi_u$ weakly in $D^{1,2}$ a.e., with $\phi_u \in D^{1,2}$.

*Step 3.*
We claim that

$$\int \nabla_x \phi_u(x) \cdot \nabla_x \xi(x) \mathrm{d}x = \int [u(x)]^2 \xi(x) \mathrm{d}x$$

for all $\xi \in D^{1,2}$. Note that $\int \nabla_x \phi_n(x) \nabla_x \xi(x) \mathrm{d}x = \int [f_n(x)]^2 \xi(x) \mathrm{d}x$ for all $\xi \in C_{\mathrm{c}}^\infty$. Indeed, as $\xi \in C_{\mathrm{c}}^\infty$ by Fubini, integration by parts and by $-\Delta_x G_{x'} = \delta_{x'}$, we have

$$\begin{aligned} \int \nabla_x \phi_n(x) \cdot \nabla_x \xi(x) \mathrm{d}x &= \int \sum_{j=1}^{3} \Big( \int \partial_j G_{x'}(x) [f_n(x')]^2 \mathrm{d}x' \Big) \partial_j \xi(x) \mathrm{d}x \\ &= \int \Big( \int G_{x'}(x) (-\Delta_x \xi(x)) \mathrm{d}x \Big) [f_n(x')]^2 \mathrm{d}x'. \end{aligned}$$

From this, $\int \nabla_x \phi_n(x) \cdot \nabla_x \xi(x) \mathrm{d}x = \int [f_n(x)]^2 \xi(x) \mathrm{d}x$ follows for all $\xi \in C_c^\infty$. Hence, since $\phi_n \longrightarrow \phi_u$ we have $\int \nabla_x \phi_u(x) \cdot \nabla_x \xi(x) \mathrm{d}x = \int [u(x)]^2 \xi(x) \mathrm{d}x$ for all $\xi \in C_c^\infty$. Since $D^{1,2} = \overline{C_c^\infty}^{\|\nabla_x \cdot\|_{L^2(\mathbb{R}^3)}}$, note that $\int \nabla_x \phi_n(x) \nabla_x \xi(x) \mathrm{d}x = \int [f_n(x)]^2 \xi(x) \mathrm{d}x$ holds for all $\xi \in D^{1,2}$.

Pick $\xi_i \xrightarrow{D^{1,2}} \xi$. Since it holds that

$$\int \nabla_x \phi_u(x) \cdot \nabla_x \xi_i(x) \mathrm{d}x = \int [u(x)]^2 \xi_i(x) \mathrm{d}x$$

and that $\int \nabla_x \phi_u(x) \cdot \nabla_x \xi_i(x) \mathrm{d}x \longrightarrow \int \nabla_x \phi_u(x) \cdot \nabla_x \xi(x) \mathrm{d}x$, we are left to show $\int [u(x)]^2 \xi_i(x) \mathrm{d}x \longrightarrow \int [u(x)]^2 \xi(x) \mathrm{d}x$. We prove that $\xi \longmapsto \int [u(x)]^2 \xi(x) \mathrm{d}x$ is a linear and continuous functional in $D^{1,2}$. To show this, we test $-\Delta_x \phi_n = f_n^2$ with $|\xi_i| \in D^{1,2}$ (which is an admissible test function, by Stampacchia's classical result): this gives

$$\int [f_n(x)]^2 |\nabla_x \xi_i(x)| \mathrm{d}x = \int \nabla_x \phi_n(x) \cdot \nabla_x (|\xi_i|)(x) \mathrm{d}x \leq \|\nabla_x \phi_n\|_{L^2} \|\nabla_x \xi_i\|_{L^2}.$$

Hence, by Fatou's Lemma, as $n \longrightarrow \infty$

$$\int [u(x)]^2 |\xi_i(x)| \mathrm{d}x \leq c \|\nabla_x \xi_i\|_{L^2}.$$

Hence, by Fatou's Lemma again and the fact that $\xi_i \longrightarrow \xi$ as $i \longrightarrow \infty$, we have that

$$\Big| \int [u(x)]^2 \xi(x) \mathrm{d}x \Big| \leq \int \big| [u(x)]^2 |\xi(x)| \big| \mathrm{d}x \leq c \|\xi\|_{D^{1,2}},$$

which completes the proof. □

### 5.1.2 Energy estimates

In this section we derive several bounds for various terms in the total energy with the range $(1, 5/3]$ for $q$, and a negative sign for $\lambda$. Eventually, we arrive at a bound for $\|\psi_k\|_{H^1}$ in terms of the total energy $E[X, \psi]$ and the electronic charge $\|\psi\|_{L^2}$.

First, we derive an estimate for the Coulombic electron-nucleus interaction energy.

Set

$$V_K[\xi](x) := -\frac{Z_K}{|x - \xi|} \text{ for } \xi, x \in \mathbb{R}^3$$

and write $V_K = V_K^1 + V_K^2$, where

$$V_K^1[\xi] = V_K[\xi]\chi_{B(\xi)}, \qquad V_K^2[\xi] = V_K[\xi][1 - \chi_{B(\xi)}].$$

Here, $\chi_{B(\xi)}$ is the characteristic function of the unit ball in $\mathbb{R}^3$, centred around $\xi$. For any fixed $\xi$, set

$$h_K[\xi](\cdot) = \min\left\{V_K^1[\xi](\cdot) - \mu, 0\right\} \leq 0.$$

**Lemma 5.4.** *For any $\varepsilon > 0$ there exists $\mu_\varepsilon < 0$ such that for all $\mu < \mu_\varepsilon$ and $k$ it holds that*

$$\sup_{\xi \in \mathbb{R}^3} \|h_K[\xi]\|_{L^{3/2}(\mathbb{R}^3;\mathbb{R})} < \varepsilon. \tag{5.5}$$

*Proof.* Setting $E_\mu[\xi] = \left\{x \in \mathbb{R}^3 \ : \ V_K^1[\xi](x) \leq \mu\right\}$ and using polar coordinates centred at $\xi$ for some uniform computable constant $C > 0$ independent of $X \in \mathbb{R}^3$ and $K$, note that

$$\begin{aligned}\|h_K[\xi]\|_{L^{3/2}(\mathbb{R}^3;\mathbb{R})}^{3/2} &= \int_{E_\mu} \left[\mu - V_K^1[\xi](x)\right]^{3/2} \mathrm{d}x \leq \int_{E_\mu} \left[ - V_K^1[\xi](x)\right]^{3/2} \mathrm{d}x \\ &= C|\mu|^{-3/2} \xrightarrow{\mu \longrightarrow -\infty} 0.\end{aligned}$$

This concludes the proof. □

**Lemma 5.5** (Lieb-type bound)**.** *Fix $X \in \mathbb{R}^{3N_{\mathrm{nuc}}}$. Let $\psi \in H^1$. For any $\varepsilon > 0$ there exists $\mu_\varepsilon < 0$ such that for all $\mu < \mu_\varepsilon$ it holds that*

$$\begin{aligned}-\sum_{K=1}^{N_{\mathrm{nuc}}} Z_K \int \frac{\rho(x)}{|x - X_K|} \mathrm{d}x \geq -\varepsilon \int |\nabla_x \psi(x)|^2 \mathrm{d}x \\ + \left(\mu N_{\mathrm{nuc}} - \sum_{K=1}^{N_{\mathrm{nuc}}} Z_K\right) \|\psi\|_{L^2}^2.\end{aligned}$$

*Proof.* By Lemma 5.4, for any $\varepsilon > 0$ there exists $\mu_\varepsilon < 0$ such that for all $\mu < \mu_\varepsilon$

$$\begin{aligned}\|h_K[X]\rho\|_{L^1} &\leq \|h_K[X]\|_{L^{3/2}} \sum_{k=1}^{N_{\mathrm{el}}} \left\|\psi_k^2\right\|_{L^3} \\ &\leq \frac{1}{S_3} \|h_K[X]\|_{L^{3/2}} \sum_{k=1}^{N_{\mathrm{el}}} \int |\nabla_x \psi_k(x)|^2 \mathrm{d}x \leq \varepsilon \int |\nabla_x \psi(x)|^2 \mathrm{d}x.\end{aligned}$$

Here, we also used Hölder's inequality (A.5) and the Sobolev inequality (A.8) on $H^1(\mathbb{R}^3)$ with Sobolev constant $S_3 = 3(\pi/2)^{4/3}$. Further, by definition of $h_K[X]$,

$$\sum_{K=1}^{N_{\text{nuc}}} \left(V_K^1[X], \rho\right)_{L^2} \geq \sum_{K=1}^{N_{\text{nuc}}} (h_K[X], \rho)_{L^2} + \mu N_{\text{nuc}} \|\rho\|_{L^1}. \tag{5.6}$$

for all $\mu < \mu_\varepsilon$. The result follows by definition of $V_K^2$. □

**Remark 5.6.** Note that the bounds in Lemmas 5.4 and 5.5 are independent of the parameter $q$.

Now, we bound the term

$$\frac{|\lambda|}{q} \int [\rho(x)]^q \mathrm{d}x,$$

which is the absolute value of the exchange energy in our generalisation for the local density approximation, for the range $q \in (1, 5/3]$ and $\lambda \neq 0$. Note that the range for $q$ contains the physically meaningful value $q = 4/3$.

**Lemma 5.7** (A Sobolev inequality)**.** *Let $\psi \in H^1$. Let $q \in (1, 5/3)$. Then, we have for all $\varepsilon > 0$*

$$\frac{|\lambda|}{q} \int [\rho(x)]^q \mathrm{d}x \leq \varepsilon \int |\nabla_x \psi(x)|^2 \mathrm{d}x + {N_{\text{el}}}^{\frac{3}{3q-5}} \left(\frac{\varepsilon q S_3}{|\lambda|}\right)^{\frac{3(q-1)}{3q-5}} \|\psi\|_{L^2}^{\frac{2(3-q)}{5-3q}}.$$

*Here, $S_3 = 3(\pi/2)^{4/3}$.*
*Furthermore, if $q = 5/3$, we have*

$$\frac{3|\lambda|}{5} \int [\rho(x)]^{5/3} \mathrm{d}x \leq \frac{3|\lambda|}{5S_3} {N_{\text{el}}}^{2/3} \|\psi\|_{L^2}^{4/3} \int |\nabla_x \psi(x)|^2 \mathrm{d}x.$$

*Proof.* Let $k \in \{1, \ldots, N_{\text{el}}\}$. By interpolation, we have

$$\|\psi_k\|_{L^{2q}} \leq \|\psi_k\|_{L^6}^{\beta} \|\psi_k\|_{L^2}^{1-\beta}$$

as long as

$$\frac{1}{2q} = \frac{\beta}{6} + \frac{1-\beta}{2}, \qquad \beta \in (0, 1).$$

This gives $\beta = 3(q-1)/(2q)$, with $1-\beta = (3-q)/(2q)$ for $q \in (1, 5/3]$. By Sobolev's inequality (A.8) on $H^1(\mathbb{R}^3)$, convexity, Young's inequality for products (A.14) with exponents $2/(3(q-1)), 2/(5-3q) > 1$ for $q \in (1, 5/3)$, we have for all $\varepsilon > 0$

$$\begin{aligned}\frac{|\lambda|}{q}\int [\rho(x)]^q \mathrm{d}x &\leq \frac{|\lambda|}{q} {N_{\mathrm{el}}}^{q-1} \sum_{k=1}^{N_{\mathrm{el}}} \|\psi_k\|_{L^{2q}}^{2q} \\ &\leq \frac{|\lambda|}{q} {N_{\mathrm{el}}}^{q-1} \sum_{k=1}^{N_{\mathrm{el}}} \left(\frac{\varepsilon q}{|\lambda| {N_{\mathrm{el}}}^{q-1}}\right)^{\frac{3(q-1)}{2}} \|\nabla_x \psi_k\|_{L^2}^{3(q-1)} \\ &\quad \times \left(\frac{\varepsilon q S_3}{|\lambda| {N_{\mathrm{el}}}^{q-1}}\right)^{-\frac{3(q-1)}{2}} \|\psi_k\|_{L^2}^{3-q} \qquad (5.7) \\ &\leq \varepsilon \|\nabla_x \psi\|_{L^2}^2 + \left(\frac{\varepsilon q S_3}{|\lambda| {N_{\mathrm{el}}}^{q-1}}\right)^{-\frac{3(q-1)}{5-3q}} \|\psi\|_{L^2}^{\frac{2(3-q)}{5-3q}}.\end{aligned}$$

If $q = 5/3$, we reduce (5.7) to

$$\begin{aligned}\frac{3|\lambda|}{5}\int [\rho(x)]^{5/3} \mathrm{d}x &\leq \frac{3|\lambda|}{5S_3} {N_{\mathrm{el}}}^{2/3} \sum_{k=1}^{N_{\mathrm{el}}} \|\nabla_x \psi_k\|_{L^2}^2 \|\psi_k\|_{L^2}^{4/3} \\ &\leq \frac{3|\lambda|}{5S_3} {N_{\mathrm{el}}}^{2/3} \|\psi\|_{L^2}^{4/3} \int |\nabla_x \psi(x)|^2 \mathrm{d}x,\end{aligned}$$

by which the result follows. □

Now, we arrive at an estimate on the total kinetic energy.

**Lemma 5.8.** *Let $\lambda < 0$, and $q \in (1, 5/3]$. Furthermore, let $T > 0$ be arbitrary. Let $X \in C^1([0,T])$ and $\psi \in C^0\big([0,T]; H^1\big)$.*

*For $1 < q < 5/3$, we have the following result. For all $0 < \varepsilon < 1/4$, there exists $\mu_\varepsilon < 0$ such that for all $\mu < \mu_\varepsilon$ it holds that for all $t \in [0,T]$*

$$\begin{aligned}&\tfrac{1}{2} \sum_{K=1}^{N_{\mathrm{nuc}}} M_K \big|\dot{X}_K(t)\big|^2 + \tfrac{1}{2}\int |\nabla_x \psi(t,x)|^2 \mathrm{d}x \leq \\ &\leq \frac{1}{1-4\varepsilon}\Big\{ E[X,\psi](t) + \Big(\sum_{K=1}^{N_{\mathrm{nuc}}} Z_K - \mu N_{\mathrm{nuc}}\Big)\|\psi(t)\|_{L^2}^2 \\ &\qquad + {N_{\mathrm{el}}}^{\frac{3}{3q-5}} \left(\frac{\varepsilon q S_3}{|\lambda|}\right)^{\frac{3(q-1)}{3q-5}} \|\psi(t)\|_{L^2}^{\frac{2(3-q)}{5-3q}} \Big\}.\end{aligned}$$

*For $q = 5/3$, we have the following result. For all $0 < \varepsilon < 1/4$, we have, provided that*

$$\frac{3|\lambda|}{5S_3} {N_{\mathrm{el}}}^{2/3} \|\psi(t)\|_{L^2}^{4/3} < \varepsilon \text{ for all } t \in [0,T], \tag{5.8}$$

*the following. There exists $\mu_\varepsilon < 0$ such that for all $\mu < \mu_\varepsilon$ it holds that for all $t \in [0,T]$*

$$\begin{aligned} &\tfrac{1}{2} \sum_{K=1}^{N_{\mathrm{nuc}}} M_K \big|\dot{X}_K(t)\big|^2 + \tfrac{1}{2} \int |\nabla_x \psi(t,x)|^2 \mathrm{d}x \leq \\ &\leq \frac{1}{1-4\varepsilon} \Big\{ E[X,\psi](t) + \Big( \sum_{K=1}^{N_{\mathrm{nuc}}} Z_K - \mu N_{\mathrm{nuc}} \Big) \|\psi(t)\|_{L^2}^2 \Big\}. \end{aligned}$$

*Proof.* For $1 < q < 5/3$, by Lemmas 5.5 and 5.7, we bound for all $0 < \varepsilon < 1/4$ the total energy (3.14) by

$$\begin{aligned} &E[X,\psi] \geq \\ &\geq \tfrac{1}{2} \sum_{K=1}^{N_{\mathrm{nuc}}} M_K \big|\dot{X}_K\big|^2 + (\tfrac{1}{2} - 2\varepsilon) \int |\nabla_x \psi(x)|^2 \mathrm{d}x + \tfrac{1}{2} \sum_{\substack{K,L=1,\\ L\neq K}}^{N_{\mathrm{nuc}}} \frac{Z_K Z_L}{|X_K - X_L|} \\ &\quad + \tfrac{1}{2} \iint \frac{\rho(x)\rho(x')}{|x-x'|} \mathrm{d}x\, \mathrm{d}x' + \Big( \mu N_{\mathrm{nuc}} - \sum_{K=1}^{N_{\mathrm{nuc}}} Z_K \Big) \|\psi\|_{L^2}^2 \\ &\quad - {N_{\mathrm{el}}}^{\frac{3}{3q-5}} \left( \frac{\varepsilon q S_3}{|\lambda|} \right)^{\frac{3(q-1)}{3q-5}} \|\psi\|_{L^2}^{\frac{2(3-q)}{5-3q}}. \end{aligned} \tag{5.9}$$

For $q = 5/3$, the proof is similar. □

Now, combining the above results, we arrive at a bound on the $H^1$ norm of the Kohn–Sham wave functions $\psi_k$, $k = 1, \ldots, N_{\mathrm{el}}$, for both cases of the range for $q$.

**Lemma 5.9.** *Let $\lambda < 0$, and $q \in (1, 5/3]$. Let $T > 0$ be arbitrary. Furthermore, let $\psi \in C^0\big([0,T]; H^1\big)$.*

*For $1 < q < 5/3$, we have the following result. For all $0 < \varepsilon < 1/4$, there exists $\mu_\varepsilon < 0$ such that for all $\mu < \mu_\varepsilon$ it holds that for all $t \in [0,T]$,*

$$\|\psi(t)\|_{H^1}^2 \leq \alpha E[X,\psi](t) + \beta \|\psi(t)\|_{L^2}^2 + \gamma \|\psi(t)\|_{L^2}^{\frac{2(3-q)}{5-3q}} \tag{5.10}$$

*with*

$$\alpha = \frac{2}{1-4\varepsilon}, \qquad \beta = 1 + \frac{2}{1-4\varepsilon}\Big(\sum_{K=1}^{N_{\mathrm{nuc}}} Z_K - \mu N_{\mathrm{nuc}}\Big),$$
$$\gamma = \frac{2}{1-4\varepsilon} {N_{\mathrm{el}}}^{\frac{3}{3q-5}} \left(\frac{\varepsilon q S_3}{|\lambda|}\right)^{-\frac{3(q-1)}{5-3q}}.$$

*For $q = 5/3$, we have the following result. For all $0 < \varepsilon < 1/4$, we have, provided that (5.8) holds, the following. There exists $\mu_\varepsilon < 0$ such that for all $\mu < \mu_\varepsilon$ it holds that for all $t \in [0, T]$*

$$\|\psi(t)\|_{H^1}^2 \leq \alpha E[X, \psi](t) + \beta \|\psi(t)\|_{L^2}^2.$$

**Remark 5.10.** Note that this bound is uniform in time, and independent of the length of our time domain $T$.

*Proof.* Lemma 5.8 implies the bound for $\|\nabla_x \psi(t)\|_{L^2}^2$ on $[0, T]$, and the result follows. □

**Remark 5.11.** Note that (5.8) boils down to the condition that $\frac{3|\lambda|}{5S_3} {N_{\mathrm{el}}}^{2/3} \|\psi^0\|_{L^2}^{4/3} < \varepsilon$ if $\psi$ enjoys charge conservation. Also, note that whenever we mention the bound (5.10) in the remainder of the thesis, we tacitly assume that this condition is met for the case $q = 5/3$.

In Appendix B.2, we derive similar estimates for the region $q \in (1, 3/2)$, which also includes the physically meaningful value $q = 4/3$. Note that the eventual $H^1$ bound there is linear with respect to the total energy and the electronic charge, while the bound for the region $q \in (1, 5/3]$ is only linear with respect to the total energy.

## 5.2 Global existence of approximated solutions

Define the Hilbert space

$$W := \Big\{\phi \in H^1(\mathbb{R}^3) \Big| \int |x|^2 |\phi(x)|^2 \mathrm{d}x < \infty\Big\} \tag{5.11}$$

equipped with the norm

$$\|\phi\|_W^2 := \|\phi\|_{H^1}^2 + \int |x|^2 |\phi(x)|^2 \mathrm{d}x$$

and the inner product

$$(\phi_1, \phi_2)_W := (\phi_1, \phi_2)_{H^1} + (|\cdot|\phi_1, |\cdot|\phi_2)_{L^2}.$$

We will study the Cauchy problem for our original system (5.1) with the initial conditions

$$\psi(0) = \psi^0 \in W, \tag{5.12}$$

$$X(0) = X^0 \in \mathbb{R}^{3N_{\text{nuc}}} \text{ with } X^0_K \neq X^0_L \text{ for } K \neq L, \tag{5.13}$$

$$\text{and } \dot{X}(0) = V^0 \in \mathbb{R}^{3N_{\text{nuc}}}, \tag{5.14}$$

To this end, we will apply by a Galerkin approximation method, inspired by the Hilbert space $W$ and the evolution equation (3.13) in the variational formulation.

First, we state some results on the Hilbert space $W$.

**Lemma 5.12.** *We have the compact embedding $W \hookrightarrow L^p(\mathbb{R}^3)$ for all $2 \leq p < 6$.*

*Proof.* Let $\mathcal{F}$ be a bounded set in $W$. By [Bre11, Prop. 9.3], we have for all $\phi \in \mathcal{F}$

$$\|\tau_h\phi - \phi\|_{L^2} \leq |h|\|\nabla_x\phi\| \leq |h|\|\phi\|_W \leq C|h|,$$

where $\tau_h$ is the translation operator $(\tau_h u)(x-h) = u(x)$. We also estimate for $M > 0$ $\phi \in \mathcal{F}$

$$\int_{|x|>M} |\phi(x)|^2 \leq \frac{1}{M^2}\int_{|x|>M} |x|^2|\phi(x)|^2 \mathrm{d}x \leq \frac{1}{M^2}\|\phi\|^2_W \leq \frac{C}{M^2}.$$

By the Riesz–Fréchet–Kolmogorov characterisation [Bre11, Cor. 4.27] the set $\mathcal{F}$ is compact in $L^2$.

This result can be extended to $p \in (2,6)$. For such $p$, let $\theta \in (0,1)$ be such that $\theta/2 + (1-\theta)/6 = 1/p$. We prove sequential compactness; let $\phi_n$ be a bounded sequence in $W$, and assume without loss of generality that $\phi_n \longrightarrow \phi$ in $L^2$ by the previous argument. Now, we bound by Hölder's inequality (A.5)

$$\begin{aligned}&\int |\phi_n(x) - \phi(x)|^p \mathrm{d}x \leq \\ &\leq \Big[\int |\phi_n(x) - \phi(x)|^2 \mathrm{d}x\Big]^{p\theta/2} \Big[\int |\phi_n(x) - \phi(x)|^6 \mathrm{d}x\Big]^{p(1-\theta)/6},\end{aligned}$$

of which the first factor tends to zero by the just proven result. As the second factor is bounded by $C$ by Sobolev's inequality (A.9), the left-hand side must tend to zero too. □

We now follow a classical construction, as in [LL01, p. 277 ff.]. Define

$$E_N := \inf \left\{ \|\phi\|_W^2 \middle| \phi \in W, \|\phi\|_{L^2} = 1, \left(\phi, \phi^\nu\right)_{L^2} = 0, \nu = 0, \dots, N-1 \right\}.$$

**Remark 5.13.** Note that by Lemma 5.12, the infimum $E_N$ is attained by some $\phi_N \in W$ with $\|\phi_N\|_{L^2} = 1$, $\left(\phi^N, \phi^\nu\right)_{L^2} = 0$ for all $\nu = 0, \dots, N-1$.

In the following, we argue as in e.g. [Jos05, Theorem 25.2, p. 362].

**Lemma 5.14** (The harmonic oscillator on $\mathbb{R}^3$)**.** *The eigenvalue problem*

$$-\Delta_x \phi + |x|^2 \phi = E\phi, \qquad x \in \mathbb{R}^3,$$

*has countably many eigenvalues with corresponding orthonormal vectors $\phi^\nu$, such that for all $\mu, \nu \in \mathbb{N}$*

$$\begin{aligned} \left(\phi^\mu, \phi^\nu\right)_{L^2(\mathbb{R}^3;\mathbb{C})} &= \delta_{\mu\nu}, \\ -\Delta_x \phi^\nu(x) + |x|^2 \phi^\nu(x) &= E_\nu \phi^\nu(x), \qquad x \in \mathbb{R}^3, \\ \left(\phi^\mu, \phi^\nu\right)_W &= E_\nu \delta_{\mu\nu}. \end{aligned}$$

*The eigenvalues $E_\nu$ are all positive, and*

$$E_\nu \xrightarrow{\nu \longrightarrow \infty} \infty.$$

*For any $\phi \in W$, we have*

$$\phi = \sum_{\nu=1}^{\infty} \left(\phi, \phi^\nu\right)_{L^2} \phi^\nu,$$

*where this series converges in $L^2$.*

*Moreover,*

$$(\phi, \phi)_W = \sum_{\nu=1}^{\infty} E_\nu \left(\phi, \phi^\nu\right)_{L^2}^2$$

*and*

$$\phi - \sum_{\nu=1}^{n} \left(\phi, \phi^\nu\right)_{L^2} \phi^\nu \xrightarrow{n \longrightarrow \infty} 0 \quad \text{in } W. \tag{5.15}$$

*Proof.* The proof follows from mild modifications to [Jos05, p. 362, Theorem 25.2]. In particular, (5.15) follows from [Jos05, p.364]. □

**Remark 5.15.** Note that from Lemma 5.14, it follows that

$$\overline{W}^{\|\cdot\|_W} = \left\{ v \in W \middle| v = \sum_{\nu=1}^{\infty} c_\nu \phi^\nu, c_\nu \in \mathbb{C} \right\} = W,$$

being the completion of $W$ under the norm on $W$ of linear combinations of $\{\phi^\nu\}_\nu \subset W$. This means

$$\left\| v - \sum_{\nu=1}^{n} c_\nu \phi^\nu \right\|_W \xrightarrow{n\longrightarrow\infty} 0.$$

Furthermore, note that $\{\phi^\nu\}_{\nu=1}^{\infty}$ forms a basis of $W$, which is orthonormal in $L^2$.

Using the above results on the space $W$, by which we know that every element of $W$ can be expressed as a (possibly infinite) linear combination of $\{\phi^\nu\}_{\nu\in\mathbb{N}}$, we want to describe the Galerkin-type approach we follow.

Note that the components of the initial condition $\psi^0 \in W$ in (5.12) can be written for all $k = 1, \dots, N_{\text{el}}$ as linear combinations

$$\psi_k^0 = \sum_{\nu=1}^{\infty} a_{k,\nu}^0 \phi^\nu, \tag{5.16}$$

with the scalar Fourier coefficients

$$a_{k,\nu}^0 = \left(\psi_k^0, \phi^\nu\right)_{L^2(\mathbb{R}^3;\mathbb{C})}, \tag{5.17}$$

for which, by Parseval's identity, it holds for all $k = 1, \dots, N_{\text{el}}$

$$\sum_{\nu=1}^{\infty} \left|a_{k,\nu}^0\right|^2 = \left\|\psi_k^0\right\|_{L^2(\mathbb{R}^3;\mathbb{C})}^2. \tag{5.18}$$

Now, we fix $n \in \mathbb{N}$. Recall the evolution equation in variational form (3.13). For all $k \in \{1, \dots, N_{\text{el}}\}$ and $\nu \in \{1, \dots, n\}$, we do the following. We set the entry $\widetilde{\psi}_k = \phi^\nu \in H^1(\mathbb{R}^3)$, with $\phi^\nu \in W$ as in Lemma 5.14, and $\widetilde{\psi}_\ell = 0$ for $1 \le \ell \ne k \le N_{\text{el}}$. Also, we put $\widetilde{X} = \widetilde{P} = 0$. Note that we perform this process $n$ times, with $n$ being the order of truncation. Furthermore, we set $\psi = \psi^n$, with elements

$$\psi_k^n(t) = \sum_{\nu=1}^{n} a_{k,\nu}^n(t) \phi^\nu \in \operatorname{span}\{\phi^\nu\}_{\nu=1}^{n} \subset W,$$

with $a^n_{k,\nu}$ time-dependent scalar coefficients of class $C^1$ in $\mathbb{C}$ and $\phi^1, \dots, \phi^n$ as in Lemma 5.14. Then, the evolution equation (3.13) yields the *approximated time-dependent Kohn–Sham equations*, which are $N_{\mathrm{el}}n$ equations, given in (5.19a).

Similarly, we do the following for all $K \in \{1, \dots, N_{\mathrm{nuc}}\}$ and $j \in \{1, 2, 3\}$. In (3.13), we put $\widetilde{X}_K = e_j \in \mathbb{R}^3$, with $e_1 = (1, 0, 0), e_2 = (0, 1, 0), e_3 = (0, 0, 1)$ the unit basis vectors of $\mathbb{R}^3$, and $\widetilde{X}_L$ for $1 \leq L \neq K \leq N_{\mathrm{nuc}}$. Also, we put $\widetilde{\psi} = 0$ and $\widetilde{P} = 0$. Then, we obtain the *approximated classical-mechanical nuclear equations* (5.19b). Together, we obtain the following system of equations:

$$\begin{aligned}
&\big(i\dot{\psi}^n_k(t), \phi^\nu\big)_{L^2} = \tfrac{1}{2}(\nabla_x \psi^n_k(t), \nabla_x \phi^\nu)_{L^2} + \\
&\left( -\sum_{K=1}^{N_{\mathrm{nuc}}} \frac{Z_K}{|x - X^n_K|}\psi^n_k(t) + \int \frac{\rho^n(t, x')}{|\cdot - x'|}\mathrm{d}x'\psi^n_k(t) - |\lambda|\big[\rho^n(t)\big]^{q-1}\psi^n_k(t), \phi^\nu \right)_{L^2},
\end{aligned} \tag{5.19a}$$

$$\ddot{X}^n_K(t) = Z_K \int \rho(t, x)\frac{\big(x - X^n_K(t)\big)}{\big|x - X^n_K(t)\big|^3}\mathrm{d}x + \sum_{L \neq K}^{N_{\mathrm{nuc}}} Z_K Z_L \frac{X^n_K(t) - X^n_L(t)}{\big|X^n_K(t) - X^n_L(t)\big|^3} \tag{5.19b}$$

for $k = 1, \dots, N_{\mathrm{el}}, K = 1, \dots, N_{\mathrm{nuc}}$ and $\nu = 1, \dots, n$. Note that in this coupled system, the elements $\psi^n$ generate elements $X^n = X^n(t), \dot{X}^n = \dot{X}^n(t)$ in the finite-dimensional phase space $\mathbb{R}^{3N_{\mathrm{nuc}}}$. Writing the shorthands $w := \big(X, \dot{X}\big)$, $w^n := \big(X^n, \dot{X}^n\big)$ and $w^0 = \big(X^0, V^0\big)$, we rewrite (5.19) to an autonomous first-order system of ordinary differential equations in terms of $\big(a^n, w^n\big)$, which is in a reduced form. Here, we choose as initial conditions

$$\psi^n(0) = \psi^{n0} = \sum_{\nu=1}^{n} a^0_{k,\nu}\phi^\nu \in W, \qquad w^n(0) = w^0 \in \mathbb{R}^{6N_{\mathrm{nuc}}}. \tag{5.20}$$

Using the orthonormality of $\phi^1, \dots, \phi^n$, we obtain the following $N_{\mathrm{el}}n +$

$2N_{\mathrm{nuc}}$ equations:

$$\begin{aligned}\dot{a}^n_{k,\mu}(t) = &-\frac{i}{2}\sum_{\nu=1}^{n} a^n_{k,\nu}(t)\int \nabla_x\phi^\nu(x)\cdot\overline{\nabla_x\phi^\mu(x)}\mathrm{d}x\\ &+ i\sum_{K=1}^{N_{\mathrm{nuc}}} Z_K\sum_{\nu=1}^{n} a^n_{k,\nu}(t)\int\frac{\phi^\nu(x)\overline{\phi^\mu(x)}}{\left|x-w^n_K\right|}\mathrm{d}x\\ &- i\iint\sum_{k'=1}^{N_{\mathrm{el}}}\Big|\sum_{\nu'=1}^{n} a^n_{k',\nu'}(t)\phi^{\nu'}(x')\Big|^2\frac{\sum_{\nu=1}^{n} a^n_{k,\nu}(t)\phi^\nu(x)\overline{\phi^\mu(x)}}{|x-x'|}\mathrm{d}x'\mathrm{d}x\\ &+ i|\lambda|\int\Big(\sum_{k'=1}^{N_{\mathrm{el}}}\Big|\sum_{\nu'=1}^{n} a^n_{k',\nu'}(t)\phi^{\nu'}(x)\Big|^2\Big)^{q-1}\sum_{\nu=1}^{n} a^n_{k,\nu}(t)\phi^\nu(x)\overline{\phi^\mu(x)}\mathrm{d}x,\end{aligned} \tag{5.21a}$$

$$\dot{w}^n_K(t) = w^n_{K+N_{\mathrm{nuc}}}(t), \tag{5.21b}$$

$$\begin{aligned}\dot{w}^n_{K+N_{\mathrm{nuc}}}(t) = \frac{Z_K}{M_K}\Bigg[&\int\frac{x-w^n_K(t)}{\left|x-w^n_K(t)\right|^3}\sum_{k=1}^{N_{\mathrm{el}}}\Big|\sum_{\nu=1}^{n} a^n_{k,\nu}(t)\phi^\nu(x)\Big|^2\mathrm{d}x\\ &+\sum_{L=1,L\neq K}^{N_{\mathrm{nuc}}} Z_L\frac{w^n_K(t)-w^n_L(t)}{\left|w^n_K(t)-w^n_L(t)\right|^3}\Bigg],\end{aligned} \tag{5.21c}$$

$$a^n_{k,\nu}(0) = a^0_{k,\nu}, \qquad w^n(0) = w^0, \tag{5.21d}$$

with the initial conditions as in (5.17) and (5.20).

We arrive at the following conservation results for the approximated solutions $\left(X^n,\psi^n\right)$ of (5.19).

**Lemma 5.16.** *Let $q\in(1,5/3]$. Let $T>0$ be arbitrary. Let $\left(\psi^n,X^n\right)$ be any solution of the system (5.19) with initial conditions (5.20) on $[0,T]$. Then the electronic charge and total energy are conserved quantities in time: that is, for all $t\in[0,T]$*

$$\left\|\psi^n(t)\right\|^2_{L^2} = \left\|\psi^{n0}\right\|^2_{L^2}, \qquad E\left[X^n,\psi^n\right](t) = E\left[X^n,\psi^n\right]\big|_{t=0}. \tag{5.22}$$

*Proof. Charge conservation.*
We write for all $k\in\{1,\dots,N_{\mathrm{el}}\}$

$$\tfrac{1}{2}\frac{\mathrm{d}}{\mathrm{d}t}\left(\left\|\psi^n_k\right\|^2_{L^2}\right) = \mathrm{Re}\int\dot{\psi}^n_k(x)\overline{\psi^n_k(x)}\mathrm{d}x. \tag{5.23}$$

Multiplying (5.19a) with $\overline{a_{k,\nu}(t)}$ and summing over $\nu = 1, \dots, n$, we identify (5.23) with the imaginary part of only purely real integrals, so equating zero. This gives charge conservation.

*Energy conservation.*
Similarly, we multiply (5.19a) with $i\overline{\dot{a}_{k,\nu}(t)}$ and sum over $\nu = 1, \dots, n$ again. We then have the imaginary part of a purely real integral at the left-hand side, so zero. We also take the dot product of the nuclear equations with $-\frac{1}{2}\dot{X}_K^n$ and sum over $K = 1, \dots, N_{\text{nuc}}$ and $k = 1, \dots, N_{\text{el}}$. Note that since $\psi^n$ is a finite sum, $\int \left|\nabla_x \psi^n(t,x)\right|^2 \mathrm{d}x$ is a second-order polynomial in the coefficients $a_{k,\nu}(t)$, which are $C^1$ functions of time by construction, giving the needed summability to perform the time differentiation. This ultimately gives, using calculations from the proof of Lemma 3.3,

$$\begin{aligned}
&-\frac{\mathrm{d}}{\mathrm{d}t}\Big(\tfrac{1}{4}\sum_{K=1}^{N_{\text{nuc}}} M_K \left|\dot{X}_K^n(t)\right|^2\Big) = \\
&= \frac{\mathrm{d}}{\mathrm{d}t}\Big[\tfrac{1}{4}\int \left|\nabla_x \psi^n(t,x)\right|^2 \mathrm{d}x - \tfrac{1}{2}\sum_{K=1}^{N_{\text{nuc}}} Z_K \int \frac{\rho^n(t,x)}{\left|x - X_K^n(t)\right|}\mathrm{d}x \\
&+ \tfrac{1}{4}\sum_{K=1}^{N_{\text{nuc}}}\sum_{L=1, L\neq K}^{N_{\text{nuc}}} \frac{Z_K Z_L}{\left|X_K^n(t) - X_L^n(t)\right|} \\
&+ \tfrac{1}{4}\iint \frac{\rho^n(t,x)\rho^n(t,x')}{|x-x'|}\mathrm{d}x\,\mathrm{d}x' - \frac{|\lambda|}{2q}\int \left[\rho^n(t,x)\right]^q \mathrm{d}x\Big]
\end{aligned} \tag{5.24}$$

which is equivalent to

$$\tfrac{1}{2}\frac{\mathrm{d}}{\mathrm{d}t}\big(E\big[X^n, \psi^n\big]\big) = 0.$$

In other words, we have conservation of the total energy of the pair $\big(X^n, \psi^n\big)$. □

Note that we write the system (5.21) as $\big(\dot{a}^n, \dot{w}^n\big) = F\big(a^n, w^n\big)$, with $F : \mathbb{R}^{2N_{\text{el}}n + 6N_{\text{nuc}}} \longrightarrow \mathbb{R}^{2N_{\text{el}}n + 6N_{\text{nuc}}}$ given by

- its first $2N_{\mathrm{el}}n$ entries

$$
\begin{aligned}
&-\frac{i}{2}\sum_{\nu=1}^{n} a_{k,\nu}^{n}\int \nabla_x\phi^{\nu}(x)\cdot\overline{\nabla_x\phi^{\mu}(x)}\mathrm{d}x\\
&+i\sum_{K=1}^{N_{\mathrm{nuc}}} Z_K\sum_{\nu=1}^{n} a_{k,\nu}^{n}\int\frac{\phi^{\nu}(x)\overline{\phi^{\mu}(x)}}{\left|x-w_K^n\right|}\mathrm{d}x\\
&-i\iint\frac{\sum_{k'=1}^{N_{\mathrm{el}}}\left|\sum_{\nu'=1}^{n} a_{k',\nu'}^{n}\phi^{\nu'}(x')\right|^2\sum_{\nu=1}^{n} a_{k,\nu}^{n}\phi^{\nu}(x)\overline{\phi^{\mu}(x)}}{|x-x'|}\mathrm{d}x'\mathrm{d}x\\
&+i|\lambda|\int\Big(\sum_{k'=1}^{N_{\mathrm{el}}}\Big|\sum_{\nu'=1}^{n} a_{k',\nu'}^{n}\phi^{\nu'}(x)\Big|^2\Big)^{q-1}\sum_{\nu=1}^{n} a_{k,\nu}^{n}\phi^{\nu}(x)\overline{\phi^{\mu}(x)}\mathrm{d}x,
\end{aligned}
\tag{5.25}
$$

  $\mu=1,\dots,n, k=1,\dots,N_{\mathrm{el}}$,

- the next $3N_{\mathrm{nuc}}$ entries

$$
w_{K+N_{\mathrm{nuc}}}^{n} \tag{5.26}
$$

  for $K=1,\dots,N_{\mathrm{nuc}}$,

- and the last $3N_{\mathrm{nuc}}$ entries

$$
\begin{aligned}
\frac{Z_K}{M_K}\Big[\int\frac{x-w_K^n}{\left|x-w_K^n\right|^3}\sum_{k=1}^{N_{\mathrm{el}}}\Big|\sum_{\nu=1}^{n} a_{k,\nu}^{n}\phi^{\nu}(x)\Big|^2\mathrm{d}x\\
+\sum_{L=1,L\neq K}^{N_{\mathrm{nuc}}} Z_L\frac{w_K^n-w_L^n}{\left|w_K^n-w_L^n\right|^3}\Big],
\end{aligned}
\tag{5.27}
$$

  for $K=1,\dots,N_{\mathrm{nuc}}$.

Note that due to the nature of the system, we regard the function mapping the space $\mathbb{R}^{2N_{\mathrm{el}}n+6N_{\mathrm{nuc}}}$ to itself by splitting the first $Nn$ equations in their real and imaginary parts, with seeing $a_{k,\nu}^{n}$ as $\big(\operatorname{Re}a_{k,\nu}^{n},\operatorname{Im}a_{k,\nu}^{n}\big)\in\mathbb{R}^2$. We use this isomorphism.

Since the nuclei are at different initial positions, we perform the following argument, in which we regard $w$ taken as a macrovector in an

open ball in $\mathbb{R}^{6N_{\mathrm{nuc}}}$.
We set

$$\delta\big(w^0\big) := \tfrac{1}{4} \min_{1\leq K\neq L\leq N_{\mathrm{nuc}}} \big|w_K^0 - w_L^0\big| > 0. \tag{5.28}$$

This defines the radius for the open ball centred around the initial configuration $w^0 \in \mathbb{R}^{6N_{\mathrm{nuc}}}$, with $w_K^0 \neq w_L^0$ for $1 \leq K \neq L \leq N_{\mathrm{nuc}}$:

$$B^n_{\delta(w^0)}\big(w^0\big) = \big\{w^n \in \mathbb{R}^{6N_{\mathrm{nuc}}} \big| \big|w^n - w^0\big| < \delta\big(w^0\big)\big\}. \tag{5.29}$$

Then, by the triangle inequality, for all $w \in B^n_{\delta(w^0)}\big(w^0\big)$ and $1 \leq K \neq L \leq N_{\mathrm{nuc}}$, the nuclei are always bounded way from each other in the Euclidean distance on $\mathbb{R}^3$, as we bound their distance from below: for all $1 \leq K \neq L \leq N_{\mathrm{nuc}}$,

$$\begin{aligned}\big\|w_K - w_L\big\|_{\mathbb{R}^3} &\geq \min_{1\leq K'\neq L'\leq N_{\mathrm{nuc}}} \big\|w_{K'}^0 - w_{L'}^0\big\|_{\mathbb{R}^3} - 2\big\|w - w^0\big\|_{\mathbb{R}^{6N_{\mathrm{nuc}}}} \\ &\geq \min_{1\leq K'\neq L'\leq N_{\mathrm{nuc}}} \big\|w_{K'}^0 - w_{L'}^0\big\|_{\mathbb{R}^3} - 2\delta\big(w^0\big) = 2\delta\big(w^0\big) > 0. \end{aligned} \tag{5.30}$$

This way, we avoid singularities for the nuclear positions.

**Lemma 5.17.** *The function $F$ as defined by (5.25)–(5.27) is continuous with respect to its arguments $\big(a^n, w^n\big)$ on the domain $\mathbb{R}^{2N_{\mathrm{el}}n} \times B^n_{\delta(w^0)}\big(w^0\big)$.*

*Proof.* We will discuss two terms in the entries of $F$ in more detail. First, we consider the second term in (5.25). Since it depends on $a^n$ only outside the integrals and in a linear sense, we restrict ourselves to dealing with the $w^n$ variable, and consider a bounded, pointwise-converging sequence $w^{n,m}(t) \xrightarrow{m\longrightarrow\infty} w^n(t)$ for all $t$; extension to a coupled sequence involving both $a^n$ and $w^n$ is then trivial. Consider the mapping

$$y \longmapsto G[\chi_1, \chi_2](y) := \int \frac{\chi_1(x)\overline{\chi_2(x)}}{|x-y|}\mathrm{d}x$$

on $\mathbb{R}^3$. If $\chi_1, \chi_2 \in C_{\mathrm{c}}^\infty\big(\mathbb{R}^3;\mathbb{C}\big)$, $G[\chi_1, \chi_2]$ is a continuous mapping in the topology of $\mathbb{R}^3$ by elliptic regularity theory. (See e.g. [LL01, Thm. 10.2 (ii), p. 260]), and [Bau+20] for more details on this mapping.) Now, we approximate the functions $\phi^\nu \in H^1\big(\mathbb{R}^3;\mathbb{C}\big)$ for $\nu = 1, \ldots, n$, by function sequences $\big\{\phi_\alpha^\nu\big\}_{\alpha\in\mathbb{N}} \subset C_{\mathrm{c}}^\infty(\mathbb{R}^3)$ such that for $\alpha \longrightarrow \infty$, $\phi_\alpha^\nu \xrightarrow{H^1(\mathbb{R}^3)} \phi^\nu$. (Note that the products $\phi_\alpha^\nu \phi_\alpha^\mu$ are elements of $C_{\mathrm{c}}^\infty\big(\mathbb{R}^3;\mathbb{C}\big)$ as well.) We

have for all $K = 1, \dots, N_{\text{nuc}}$

$$\begin{aligned}
&\left|G\left[\phi^\mu, \phi^\nu\right]\left(w_K^{n,m}\right) - G\left[\phi^\mu, \phi^\nu\right]\left(w_K^n\right)\right| \leq \\
&\leq \left|G\left[\phi^\mu, \phi^\nu\right]\left(w_K^{n,m}\right) - G\left[\phi_\alpha^\mu, \phi_\alpha^\nu\right]\left(w_K^{n,m}\right)\right| \\
&\quad + \left|G\left[\phi_\alpha^\mu, \phi_\alpha^\nu\right]\left(w_K^{n,m}\right) - G\left[\phi_\alpha^\mu, \phi_\alpha^\nu\right]\left(w_K^n\right)\right| \\
&\quad + \left|G\left[\phi_\alpha^\mu, \phi_\alpha^\nu\right]\left(w_K^n\right) - G\left[\phi^\mu, \phi^\nu\right]\left(w_K^n\right)\right|.
\end{aligned}$$

Now, the first and the third term on the right-hand side go to 0 for $\alpha \longrightarrow \infty$ using Hardy's inequality (A.4) together with the fact that $\phi_\alpha^\nu \xrightarrow{H^1(\mathbb{R}^3)} \phi^\nu$. The second term goes to 0 for $m \longrightarrow \infty$ for all $\alpha \in \mathbb{N}$ as $G\left[\phi_\alpha^\mu, \chi_\alpha^\nu\right]$ is continuous in the topology of $\mathbb{R}^3$. By this, the left-hand side also goes to 0 for $m \longrightarrow \infty$, which concludes the continuity of the second term in (5.25).

Secondly, we consider the first term in (5.27). Note that the dependence on $a^n$ is quadratic, yet inside the integrals; by expanding the squares we place it outside, and again restrict ourselves to dealing with the variable $w^n$ only. The expansions are in terms of the mapping

$$y \longmapsto D[\chi_1, \chi_2](y) := \int \frac{x-y}{|x-y|^3} \chi_1(x) \overline{\chi_2(x)} \mathrm{d}x$$

on $\mathbb{R}^3$, and we conclude the continuity of this term fully analogously as above for the mapping $D$.

The third and fourth term in (5.25) can be treated using the dominated convergence theorem for a bounded, pointwise-converging sequence $a^n$ in $\mathbb{R}^{2N_{\text{el}}n}$. The second term in (5.27) is continuous in the topology of $\mathbb{R}^{6N_{\text{nuc}}}$ on $B_{\delta(w^0)}\left(w^0\right)$ by definition: see (4.53). The remaining terms in the entries of $F$, viz. the first term in (5.25) and the term in (5.26), are linear in $a^n$ resp. $w^n$. We conclude the proof. □

**Lemma 5.18** (Global existence of solutions to the truncated problem)**.** *For all fixed $n \in \mathbb{N}$, there exists a solution $\left(a^n, w^n\right)$ defined on the entire half-line $[0, +\infty)$ to the Cauchy problem (5.21).*

*Proof. Part 1. Existence.*
We consider $F$ on the domain $\mathbb{R}^{2N_{\text{el}}n} \times B_{\delta(w^0)}^n\left(w^0\right)$. Since $F$ is continuous on this set in the topology of $\mathbb{R}^{2N_{\text{el}}n+6N_{\text{nuc}}}$ by Lemma 5.17, by Peano existence theorem, we know there exists $T_{n,\max} > 0$ such that there exists a local solution to the Cauchy problem on $[0, T_{n,\max})$.

*Part 2. Boundedness of $F$ along solution trajectories.*
From part 1, we know we have a solution on a certain non-trivial time interval. We first can prove that $F\big(a^n(t), w^n(t)\big)$ remains bounded in the according trajectory $\big(t, a^n(t), w^n(t)\big)$ on that time interval. We bound the absolute value $\big|F\big(a^n(t), w^n(t)\big)\big|$ taken in $\mathbb{R}^{2N_{\mathrm{el}}n+6N_{\mathrm{nuc}}}$ by the absolute value of all separate entries in $\mathbb{R}$, using the triangular inequality. Furthermore, we use the conservation of charge and energy for the approximated solutions $\big(\psi^n, X^n\big)$ as proven in Lemma 5.16, together with the Coulomb–Sobolev bound as proven in Lemma 5.9 for $\psi^n$, as it solves the original approximated TDKS equations.

For the first entries of $F\big(a^n(t), w^n(t)\big)$, we first note that, using Cauchy–Schwarz, the modulus of the first terms can be bounded for all $\mu = 1, \dots, n$ by

$$\begin{aligned}\tfrac{1}{2}\sum_{k=1}^{N_{\mathrm{el}}}\Big|\int\sum_{\nu=1}^{n} a^n_{k,\nu}(t)\nabla_x\phi^\nu(x)\overline{\nabla_x\phi^\mu(x)}\mathrm{d}x\Big| &\leq \sum_{k=1}^{N_{\mathrm{el}}}\big|\big(\nabla_x\psi^n_k(t), \nabla_x\phi^\mu\big)_{L^2}\big| \\ &\leq \sum_{k=1}^{N_{\mathrm{el}}}\big\|\nabla_x\psi^n_k\big\|_{L^2}\big\|\nabla_x\phi^\mu\big\|_{L^2} \leq \big\|\psi^n(t)\big\|_{H^1}\big\|\nabla_x\phi^\mu\big\|_{L^2},\end{aligned}$$

and the modulus of the second terms, using Cauchy–Schwarz, Hardy's inequality (A.4) and orthonormality of $\phi^1, \dots, \phi^n$, similarly by

$$\begin{aligned}&\sum_{k=1}^{N_{\mathrm{el}}}\Big|\sum_{K=1}^{N_{\mathrm{nuc}}} Z_K\int\frac{\sum_{\nu=1}^{n} a^n_{k,\nu}(t)\phi^\nu(x)\overline{\phi^\mu(x)}}{\big|x - w^n_K(t)\big|}\mathrm{d}x\Big| \leq \\ &\quad\leq C\sum_{k=1}^{N_{\mathrm{el}}}\sum_{K=1}^{N_{\mathrm{nuc}}}\big|\big(\big|\cdot - w^n_K(t)\big|^{-1}\psi^n_k(t), \phi^\mu\big)_{L^2}\big| \\ &\quad\leq C\sum_{k=1}^{N_{\mathrm{el}}}\sum_{K=1}^{N_{\mathrm{nuc}}}\big\|\big|\cdot - w^n_K(t)\big|^{-1}\psi^n_k(t)\big\|_{L^2}\big\|\phi^\mu\big\|_{L^2} \\ &\quad\leq 2CN_{\mathrm{nuc}}\big\|\nabla_x\psi^n(t)\big\|_{L^2} \leq 2CN_{\mathrm{nuc}}\big\|\psi^n(t)\big\|_{H^1}\end{aligned}$$

where $C$ is independently of $w^n$.

For the third term, we apply the Hardy–Littlewood–Sobolev inequality (A.7) with $\alpha = 1, n = 3, p = r = 6/5$, and $f = \sum_{k'=1}^{N_{\mathrm{el}}}\big|\psi^n_{k'}(t)\big|^2, g = \psi^n_k\overline{\phi^\mu}$. Using this together with Hölder's (A.5) and Sobolev's inequality with interpolation in Corollary A.8, we bound the modulus of the third

terms as

$$\sum_{k=1}^{N_{\mathrm{el}}}\Big|\iint\frac{\sum_{k'=1}^{N_{\mathrm{el}}}\Big|\sum_{\nu'=1}^{n}a^n_{k',\nu'}(t)\phi^{\nu'}(x')\Big|^2\sum_{\nu=1}^{n}a^n_{k,\nu}(t)\phi^{\nu}(x)\overline{\phi^{\mu}(x)}}{|x-x'|}\mathrm{d}x'\mathrm{d}x\Big| =$$
$$=\sum_{k=1}^{N_{\mathrm{el}}}\Big|\iint\frac{\sum_{k'=1}^{N_{\mathrm{el}}}\big|\psi^n_{k'}(t,x')\big|^2\psi^n_k(t,x)\overline{\phi^{\mu}(x)}}{|x-x'|}\mathrm{d}x'\mathrm{d}x\Big|$$
$$\le C\Big[\int\Big(\sum_{k'=1}^{N_{\mathrm{el}}}\big|\psi^n_{k'}(t,x)\big|^2\Big)^{6/5}\mathrm{d}x\Big]^{5/6}\sum_{k=1}^{N_{\mathrm{el}}}\Big[\int\big[\psi^n_k(t,x)\overline{\phi^{\mu}(x)}\big]^{6/5}\mathrm{d}x\Big]^{5/6}$$
$$\le C'\sum_{k'=1}^{N_{\mathrm{el}}}\big\|\psi^n_{k'}(t)\big\|^2_{L^{12/5}(\mathbb{R}^3;\mathbb{C})}\sum_{k=1}^{N_{\mathrm{el}}}\big\|\psi^n_k(t)\big\|_{L^{12/5}(\mathbb{R}^3;\mathbb{C})}\big\|\phi^{\mu}\big\|_{L^{12/5}(\mathbb{R}^3;\mathbb{C})}$$
$$\le C''\big\|\psi^n\big\|^3_{H^1}\big\|\phi^{\mu}\big\|_{H^1}$$

The modulus of the last terms can be bounded, using that $q\in[2,6)$ together with the generalised Hölder's inequality (see (A.5)) with $d=3$ and exponents $p_1=q/(q-1)$, $p_2=p_3=2q$ and $f_1=\big[\sum_{k'=1}^{N_{\mathrm{el}}}\big|\psi^n_{k'}\big|^2\big]^{q-1}$, $f_2=\psi^n_k(t)$, $f_3=\overline{\phi^{\mu}}$, and Sobolev's inequality with interpolation in Corollary A.8 by

$$|\lambda|\sum_{k=1}^{N_{\mathrm{el}}}\Big|\int\Big[\sum_{k'=1}^{N_{\mathrm{el}}}\Big|\sum_{\nu'=1}^{n}a^n_{k',\nu'}(t)\phi^{\nu'}(x)\Big|^2\Big]^{q-1}\sum_{\nu=1}^{n}a^n_{k,\nu}(t)\phi^{\nu}(x)\overline{\phi^{\mu}(x)}\mathrm{d}x\Big|\le$$
$$\le C_q|\lambda|\sum_{k'=1}^{N_{\mathrm{el}}}\big\|\psi^n_k(t)\big\|^{(q-1)/2q^2}_{L^{2q}}\sum_{k=1}^{N_{\mathrm{el}}}\big\|\psi^n_j(t)\big\|_{L^{2q}}\big\|\phi^{\mu}\big\|_{L^{2q}}$$
$$\le C'_q|\lambda|\big\|\psi^n(t)\big\|^{(q^2+q/2-1)/q^2}_{H^1}\big\|\phi^{\mu}\big\|_{H^1}.$$

For the other entries of $F\big(a^n(t),w^n(t)\big)$, we apply a Grönwall argument based on nuclear repulsion just like as in Section 4.4. Writing

$$\mathcal{H}_{\mathrm{nn}}(w):=\tfrac{1}{2}\sum_{K=1}^{N_{\mathrm{nuc}}}\frac{|w_{K+N_{\mathrm{nuc}}}|^2}{M_K}+W_{\mathrm{nn}}(w),$$
$$W_{\mathrm{nn}}(w):=\tfrac{1}{2}\sum_{\substack{K,L=1,\\L\neq K}}^{N_{\mathrm{nuc}}}\frac{Z_KZ_L}{|w_K-w_L|},$$

we have, as $w^n$ satisfies (5.19b),

$$\begin{aligned}
&\frac{\mathrm{d}}{\mathrm{d}t}\big[\mathcal{H}_{\mathrm{nn}}\big(w^n\big)\big](t) = \\
&= \sum_{K=1}^{N_{\mathrm{nuc}}} \big[\nabla_{w_K}\mathcal{H}_{\mathrm{nn}}\big(w^n(t)\big)\cdot w^n_{K+N_{\mathrm{nuc}}}(t) \\
&\quad + \nabla_{w_{K+N_{\mathrm{nuc}}}}\mathcal{H}_{\mathrm{nn}}\big(w^n(t)\big)\cdot \dot{w}^n_{K+N_{\mathrm{nuc}}}(t)\big] \\
&= \sum_{K=1}^{N_{\mathrm{nuc}}} w^n_{K+N_{\mathrm{nuc}}}(t)\cdot\big\{\nabla_{w_K}\big[W_{\mathrm{nn}}\big(w^n(t)\big)\big] + M_K\dot{w}^n_{K+N_{\mathrm{nuc}}}(t)\big\} \\
&= -\sum_{K=1}^{N_{\mathrm{nuc}}} \frac{Z_K}{M_K} w^n_{K+N_{\mathrm{nuc}}}(t)\cdot\left(\frac{\cdot - w^n_K(t)}{|\cdot - w^n_K(t)|^3}, \sum_{k=1}^{N_{\mathrm{el}}}|\psi^n_k(t)|^2\right)_{L^2} \\
&\leq \sum_{K=1}^{N_{\mathrm{nuc}}} \frac{1}{2M_K}\big[|w^n_{K+N_{\mathrm{nuc}}}(t)|^2 + Z_K\big\||\cdot - w^n_K(t)|^{-1}\psi^n_k(t)\big\|^2_{L^2}\big] \\
&\leq \mathcal{H}_{\mathrm{nn}}\big(w^n(t)\big) + 8\sum_{K=1}^{N_{\mathrm{nuc}}}\frac{Z_K^2}{M_K}\big\|\psi^n(t)\big\|^2_{H^1} \leq \mathcal{H}_{\mathrm{nn}}\big(w^n(t)\big) + C, \qquad (5.31)
\end{aligned}$$

by which, using Grönwall's inequality (A.15), on $[0, T_{n,\max}]$, with $T_{n,\max} > 0$ denoting the length of the time interval on which the solution we found in part 1 exists,

$$\begin{aligned}
&\mathcal{H}_{\mathrm{nn}}\big(w^n(t)\big) \leq \\
&\leq \tfrac{1}{2}e^{T_{n,\max}}\left[\sum_{K=1}^{N_{\mathrm{nuc}}} M_K|V^0_K|^2 + \sum_{\substack{K,L=1,\\ L\neq K}}^{N_{\mathrm{nuc}}}\frac{Z_KZ_L}{|X^0_K - X^0_L|} + 16\sum_{K=1}^{N_{\mathrm{nuc}}}\frac{Z_K^2}{M_K}\|\psi(t)\|^2_{H^1}\right] \\
&\quad - 8\sum_{K=1}^{N_{\mathrm{nuc}}}\frac{Z_K^2}{M_K}\big\|\psi^n(t)\big\|^2_{H^1}. \qquad (5.32)
\end{aligned}$$

Here we used Young's inequality for products (A.14) along with Hardy's inequality (A.4).
Now, the modulus of the second entries of $F\big(a^n(t), w^n(t)\big)$ can be bounded as

$$\sum_{K=1}^{N_{\mathrm{nuc}}}|w^n_{K+N_{\mathrm{nuc}}}(t)| \leq C(M)\mathcal{H}_{\mathrm{nn}}\big(w^n(t)\big)^{1/2},$$

and the modulus of the third entries of $F\big(a^n(t), w^n(t)\big)$ can be bounded (see Lemma 4.11, the proof of Lemma 4.20 and (4.53)) by

$$\sum_{K=1}^{N_{\mathrm{nuc}}} \frac{Z_K}{M_K} \Bigg[ \Bigg| \int \frac{\cdot - w_K^n(t)}{|\cdot - w_K^n(t)|} \sum_{k=1}^{N_{\mathrm{el}}} \big|a_{k,\nu}^n(t)\phi^\nu(x)\big|^2 \mathrm{d}x + \sum_{L=1, L\neq K}^{N_{\mathrm{nuc}}} Z_L \frac{w_K^n(t) - w_L^n(t)}{\big|w_K^n(t) - w_L^n(t)\big|^3} \Bigg| \Bigg]$$
$$\leq C_1 \big\|\nabla_x \psi^n(t)\big\|_{L^2}^2 + C_2 W_{\mathrm{nn}}\big(w^n(t)\big) \leq C_1 \big\|\psi^n(t)\big\|_{H^1}^2 + C_2 \mathcal{H}_{\mathrm{nn}}\big(w^n(t)\big)$$

where $C_1, C_2$ are independent of $w^n$. Altogether, we bound $\big|F\big(a^n(t), w^n(t)\big)\big|$, using (5.10), on $[0, T_{n,\max})$ as

$$\begin{aligned}
&\big|F\big(a^n(t), w^n(t)\big)\big| \lesssim_{q,\lambda} \\
&\lesssim_{q,\lambda} \Big\{ \|\psi^n(t)\|_{H^1}^2 + \Big( \|\psi^n(t)\|_{H^1} + \|\psi^n(t)\|_{H^1}^3 + \|\psi^n(t)\|_{H^1}^{(q^2+q/2-1)/q^2} \Big) \times \\
&\quad \times \sum_{\mu=1}^{n} \|\phi^\mu\|_{H^1} + \mathcal{H}_{\mathrm{nn}}\big(w^n(t)\big)^{1/2} + \mathcal{H}_{\mathrm{nn}}\big(w^n(t)\big) \Big\} \\
&\leq C_q'\big(n, \mathcal{H}_{\mathrm{nn}}\big(w^n(t)\big), \|\psi^n(t)\|_{H^1}\big)
\end{aligned}$$

Note that we have the conservation of charge and energy as proven in Lemma 5.16 for the approximated solution $\psi^n$, and that it satisfies the $H^1$ bound from Lemma 5.9, which also appears in the Grönwall bounds for $\mathcal{H}_{\mathrm{nn}}\big(w^n(t)\big)$. This ensures that $\big|F\big(a^n(t), w^n(t)\big)\big|$ indeed remains bounded along the trajectory of the solution $\big(a^n(t), w^n(t)\big)$ on $[0, T_{n,\max}]$.

*Part 3. Global existence.*
The reasoning follows a proof by contradiction: we start by assuming there is no global solution to the Cauchy problem. However, by part 1 we know there exists a solution $\big(a^n, w^n\big)$ on a non-trivial time interval $[0, T_{n,\max})$. Our assumption then implies that this solution is non-extendible: it cannot be extended beyond the finite end point $T_{n,\max} < +\infty$.

We argue as in [CL55, pp. 13–15]. Remember that $F$ is continuous on $\mathbb{R}^{2N_{\mathrm{el}}n} \times B_{\delta(w^0)}\big(w^0\big)$ with respect to $(a, w)$ in the $\mathbb{R}^{2N_{\mathrm{el}}n+6N_{\mathrm{nuc}}}$ topology, and that by part 1 the Cauchy problem has a solution $\big(a^n, w^n\big)$ on a finite interval $[0, T_{n,\max}]$. Since $\big|F\big(a^n, w^n\big)\big|$ is bounded by a constant $M < \infty$ on $[0, T_{n,\max})$, the left limit

$$\big(a_*^n, w_*^n\big) := \lim_{t \uparrow T_{n,\max}} \big\{\big(a^n(t), w^n(t)\big)\big\}$$

exists. This can be seen, as the integral formulation for $t \in [0, T_{n,\max})$

$$\big(a^n(t), w^n(t)\big) = \big(a^0, w^0\big) + \int_0^t F\big(a^n(t'), w^n(t')\big)\mathrm{d}t'$$

gives for $0 < t_1 < t_2 < T_{n,\max}$

$$\begin{aligned}&\big\|\big(a^n(t_1), w^n(t_1)\big) - \big(a^n(t_2), w^n(t_2)\big)\big\|_{\mathbb{R}^{2N_{\mathrm{el}}n+6N_{\mathrm{nuc}}}} \leq \\ &\leq \int_{t_1}^{t_2} \big\|F\big(a^n(t'), w^n(t')\big)\big\|_{\mathbb{R}^{2N_{\mathrm{el}}n+6N_{\mathrm{nuc}}}}\mathrm{d}t' \leq M|t_1 - t_2|,\end{aligned}$$

by which

$$\big(a^n(t_1), w^n(t_1)\big) - \big(a^n(t_2), w^n(t_2)\big) \xrightarrow{t_1,t_2\uparrow T_{n,\max}} 0.$$

This implies by the Cauchy convergence criterion that the left limit exists indeed.

Now, we extend the solution beyond the supposed endpoint of the time domain $T_{n,\max}$, which will lead to a contradiction.
As for the solution trajectory $\big(a^n, w^n\big)$ on $[0, T_{n,\max}]$, it holds that for $1 \leq K \neq L \leq N_{\mathrm{nuc}}$

$$\frac{1}{\big|w_K^n(t) - w_L^n(t)\big|} \leq W_{\mathrm{nn}}\big(w^n(t)\big) \leq \mathcal{H}_{\mathrm{nn}}\big(w^n(t)\big),$$

which is bounded by (5.31). So, we know the nuclei stay bounded away from each other on the time interval. Also, $T_{n,\max}$ is finite; by this, we consider a shifted Cauchy problem on a different open ball $B_{\delta'}\big(w_*^n\big) \subset \mathbb{R}^{6N_{\mathrm{nuc}}}$, with $\delta' = \delta\big(w_*^n\big) = \frac{1}{4}\min_{1\leq K\neq L\leq N_{\mathrm{nuc}}}\big|w_{*,K}^n - w_{*,L}^n\big|$. We know $\big(a_*^n, w_*^n\big)$ belongs to the open domain $\mathbb{R}^{2N_{\mathrm{el}}n} \times B_{\delta'}\big(w_*^n\big)$, as $F$ is continuous with respect to $a^n$ everywhere in the $\mathbb{R}^{2N_{\mathrm{el}}n}$ topology, and, as the nuclei stay bounded away from each other, there are no singularities in $w^n$. So, $F$ is also continuous with respect to $w^n$ on this new domain in the $\mathbb{R}^{6N_{\mathrm{nuc}}}$ topology. This shifted Cauchy problem reads

$$\big(\dot{a}^n, \dot{w}^n\big) = F\big(a^n, w^n\big), \qquad \big(a^n(T_{n,\max}), w^n(T_{n,\max})\big) = \big(a_*^n, w_*^n\big).$$

Now, we apply the Peano existence theorem on the shifted problem, by which this problem has a continuously differentiable solution, which we call $\big(\widetilde{a}^n, \widetilde{w}^n\big)$, on $[T_{n,\max}, T_{n,\max} + \beta]$ for some $\beta > 0$. Now, we glue

the two solutions we found together, by which we obtain the extended solution

$$\begin{cases} \big(\widehat{a}^n, \widehat{w}^n\big) & := \big(a^n, w^n\big) \text{ on } [0, T_{n,\max}], \\ \big(\widehat{a}^n, \widehat{w}^n\big) & := \big(\widetilde{a}^n, \widetilde{w}^n\big) \text{ on } [T_{n,\max}, T_{n,\max} + \beta]. \end{cases}$$

Now, $\big(\widehat{a}^n, \widehat{w}^n\big)$ solves the original Cauchy problem (5.21)–(5.21d) on $[0, T_{n,\max} + \beta]$. Here, the only thing to check is existence and continuity with respect to time at $T_{n,\max}$ of the derivative $\big(\dot{\widehat{a}}^n, \dot{\widehat{w}}^n\big)$. We then must have for all $t \in [0, T_{n,\max} + \beta]$

$$\big(\widehat{a}^n(t), \widehat{w}^n(t)\big) = \big(a^0, w^0\big) + \int_0^t F\big(\widehat{a}^n(t'), \widehat{w}^n(t')\big) \mathrm{d}t'. \tag{5.33}$$

For $t \in [0, T_{n,\max}]$, this is treated in part 1. For $t > T_{n,\max}$, (5.33) follows from

$$\begin{aligned} \big(\widehat{a}^n(t), \widehat{w}^n(t)\big) &= \big(a_*^n, w_*^n\big) + \int_{T_{n,\max}}^t F\big(\widehat{a}^n(t'), \widehat{w}^n(t')\big) \mathrm{d}t', \\ \big(a_*^n, w_*^n\big) &= \big(a^0, w^0\big) + \int_0^{T_{n,\max}} F\big(\widehat{a}^n(t'), \widehat{w}^n(t')\big) \mathrm{d}t'. \end{aligned}$$

The continuity of $\big(\widehat{a}^n, \widehat{w}^n\big)$ in (5.33) implies the continuity of $F\big(\widehat{a}^n, \widehat{w}^n\big)$; differentiating the integral equation (5.33) then gives the fact that $\big(\dot{\widehat{a}}^n(t), \dot{\widehat{w}}^n(t)\big) = F\big(\widehat{a}^n(t), \widehat{w}^n(t)\big)$ for $t \in [0, T_{n,\max} + \beta]$. Now, we have proven that $\big(\widehat{a}^n, \widehat{w}^n\big)$ is an extension of the solution $\big(a^n, w^n\big)$ beyond $T_{n,\max}$. This contradicts the maximality of $T_{n,\max}$. By this, $T_{n,\max}$ has to be equal to $+\infty$, and there exists a global solution to the original Cauchy problem (5.21)–(5.21d). □

**Remark 5.19.** Note that since there is a global solution $\big(a^n, w^n\big)$, this induces a global solution $\big(\psi^n, X^n\big) \in C^1\big([0,T]; H^1\big) \times C^2\big([0,T]; \mathbb{R}^{3N_{\mathrm{nuc}}}\big)$ for arbitrary $T > 0$ to (5.19), for which the total energy and electronic charge are conserved, as shown in Lemma 5.16.

Furthermore, by linearity, in (3.13), instead of an eigenfunction $\phi^\nu$, $\nu = 1, \dots, n$, we could have chosen any generic element $\widetilde{\psi}_k = v \in \operatorname{span}\big\{\phi^\nu\big\}_{\nu=1}^n$ for (5.19a), as $v$ can always be expanded as a linear combination

$$v(t,x) = \sum_{\nu=1}^n c_\nu(t) \phi^\nu(x).$$

Then, by linearity, separation of variables and integration by parts, the resulting solution $\big(\psi^n, X^n\big)$ to those equations using $v$ also satisfies the weak formulation (5.3) in a weak sense, in a pointwise way. This implies that the system (5.3) is solved with $\psi^n \in C^1\big([0,T]; H^1\big)$ for all $v \in L^2H^1$, where $v$ can be expanded as above.

## 5.3 Towards existence of weak solutions

In this section, we prove the main result of this chapter, Theorem 5.2, under Conjecture 5.1. To this end, we use compactness and convergence results, partly inspired by [Sim86].

**Lemma 5.20.** *For fixed $n \in \mathbb{N}$ and arbitrary $T > 0$, let $\psi^n$ be a solution of (5.19a) on the time domain $[0,T]$. Then, its second moment*

$$\int |x|^2 |\psi^n(t,x)|^2 \mathrm{d}x.$$

*satisfies the bound*

$$\int |x|^2 |\psi^n(t,x)|^2 \mathrm{d}x \leq e^t \int |x|^2 \big|\psi^{n0}(x)\big|^2 \mathrm{d}x + \int_0^t e^{t-t'} \|\nabla_x \psi^n(t')\|_{L^2}^2 \mathrm{d}t'$$

*for all $t \in [0,T]$.*

*Proof.* We have that

$$\partial_t \Big[ \int |x|^2 |\psi^n(t,x)|^2 \mathrm{d}x \Big] = 2 \int |x|^2 \mathrm{Re}\big[\overline{\psi^n(t,x)} \dot{\psi^n}(t,x)\big] \mathrm{d}x.$$

Since $\psi^n$ satisfies (5.19a), this is equal to

$$\mathrm{Re}\Big[ i \int |x|^2 \overline{\psi^n(t,x)} \Delta_x \psi^n(t,x) \mathrm{d}x \Big] + \underbrace{2\mathrm{Re}\Big[ i \sum_{K=1}^{N_{\mathrm{nuc}}} Z_K \int \frac{|x|^2 |\psi^n(t,x)|^2}{|x - X_K|} \mathrm{d}x \Big]}_{=0}$$

$$- \underbrace{2\mathrm{Re}\Big[ i \iint \frac{|x|^2 \rho(t,x) \rho(t,x')}{|x - x'|} \mathrm{d}x \mathrm{d}x' \Big]}_{=0} - \underbrace{2\mathrm{Re}\Big[ i\lambda \int |x|^2 [\rho(t,x)]^q \mathrm{d}x \Big]}_{=0}.$$

Using Green's first identity, we can write this as

$$\begin{aligned}
&\frac{i}{2}\int |x|^2\big[\overline{\psi^n(t,x)}\Delta_x\psi^n(t,x) - \psi^n(t,x)\Delta_x\overline{\psi^n(t,x)}\big]\mathrm{d}x = \\
&= -\frac{i}{2}\int \big[\nabla_x\big(|x|^2\overline{\psi^n}\big)(t,x)\cdot\nabla_x\psi^n(t,x) \\
&\quad - \nabla_x\big(|x|^2\psi^n\big)(t,x)\cdot\nabla_x\overline{\psi^n}(t,x)\big]\mathrm{d}x \\
&= -i\int x\cdot\big[\overline{\psi^n}(t,x)\nabla_x\psi^n(t,x) - \psi^n(t,x)\nabla_x\overline{\psi^n}(t,x)\big]\mathrm{d}x.
\end{aligned}$$

By Young's inequality for products (A.14), we get

$$\begin{aligned}
\Big|\partial_t\Big[\int |x|^2|\psi^n(t,x)|^2\mathrm{d}x\Big]\Big| &\le 2\big\|\nabla_x\psi^n(t)\big\|_{L^2}\big\||\cdot|\psi^n(t)\big\|_{L^2} \\
&\le \big\|\nabla_x\psi^n(t)\big\|_{L^2}^2 + \big\||\cdot|\psi^n(t)\big\|_{L^2}^2.
\end{aligned}$$

The result follows by Grönwall's inequality (A.15). □

**Lemma 5.21.** *Let $\{\psi^n\}_{n\in\mathbb{N}}$ denote a sequence of solutions of (5.19a). Then this sequence enjoys the following bounds:*

$$\big\|\psi^n\big\|_{L^\infty((0,T);W^{N_{\mathrm{el}}})} + \big\|\dot{\psi}^n\big\|_{L^\infty((0,T);(W^*)^{N_{\mathrm{el}}})} \le C,$$

*Here $C$ is independent of $n$.*

*Proof.* Since $\psi^n(t)$ is an element of $\operatorname{span}\{\phi^\nu\}_{\nu=1}^n \subset W^{N_{\mathrm{el}}}$ for all $t \in [0,T]$, it is an element of $L^\infty\big(0,T;W^{N_{\mathrm{el}}}\big)$. By Lemma 5.16, the total energy and charge are conserved. By Lemma 5.9, $\big\|\nabla_x\psi^n(t)\big\|_{L^2}$ is bounded on $[0,T]$. By Lemma 5.20, $\big\||\cdot|\psi^n\big\|_{L^2}$ is bounded as well. Together, this yields the bound $\big\|\psi^n\big\|_{L^\infty((0,T);W^{N_{\mathrm{el}}})} \le C$.

For $\dot{\psi}_n$, we discuss the terms on the right-hand side of (5.19a) one by one; if these four terms are elements of some space $L^\infty((0,T);E_j)$, $j\in\{1,2,3,4\}$, then

$$\dot{\psi}^n \in L^\infty(0,T;E_1+E_2+E_3+E_4).$$

For the Laplacian term, we know that for all $t\in[0,T]$

$$\Delta_x\psi^n(t) \in H^{-1} =: E_1.$$

By Hardy's inequality (A.4), for the external potential term it holds for all $t\in[0,T]$ that

$$\frac{\psi^n(t)}{|\cdot - X_K^n(t)|} \in L^2 =: E_2.$$

By Sobolev's inequality (A.9), since for all $t \in [0,T]$, $\psi^n(t)$ is bounded in $H^1$, we know that $\psi^n(t) \in L^6 \cap L^2$ and thus $\rho^n(t) \in L^3 \cap L^1$. By this, $|\cdot|^{-1} * \rho^n(t) \in L^6$, and the convolution term then, by Hölder's inequality (A.5), for all $t \in [0,T]$

$$\big(|\cdot|^{-1} * \rho^n(t)\big)\psi^n(t) \in L^3 =: E_3.$$

We know that for all $t \in [0,T]$, $\rho^n(t) \in L^q$, so $\psi^n(t) \in L^{2q}$. Further, we know that as $\psi^n(t) \in H^1$, $\psi^n(t) \in L^p$ for all $p \in [2,6]$ as well. Now, as $q \in (1,5/3]$, $2(2q-1) \in (2,14/3] \subset [2,6]$. This gives for the exchange term

$$\big|\rho^{n,q-1}(t)\psi^n(t)\big| = \big|\psi^n(t)\big|^{2q-1} \in L^2 = E_4 = E_2.$$

Altogether, we have that $\dot{\psi}^n \in L^\infty((0,T);E)$ for every $n$, with

$$E := H^{-1} + L^2 + L^3.$$

Now, since $W \subset H^1$, $H^{-1} = \big(H^1\big)^* \subset W^*$. Indeed, for all $\xi \in H^{-1}$ and $\phi \in W$, we see that the product, since $\|\cdot\|_{H^1} \leq \|\cdot\|_W$,

$$|{}_{H^{-1}}\langle \xi, \phi \rangle_{H^1}| \leq C\|\xi\|_{H^{-1}}\|\phi\|_W,$$

by which $H^{-1} \hookrightarrow W^*$ continuously.

Since $L^2 = \big(L^2\big)^*$ and $W \subset L^2 = E_2$, and by Lemma 5.12 $W \subset L^3 = E_3$, it follows that the terms $E_2$ and $E_3$ of $E$ are continuously embedded in $W^*$ similarly as for the Laplacian term $E_1$.

Eventually, we obtain for the right-hand side terms in the first equations in (5.3)

$$\big|\big(\nabla_x\psi_k^n, \nabla_x v\big)_{L^2}\big| \leq C\big\|\nabla_x\psi^n\big\|_{L^2}\|\nabla_x v\|_{L^2} \leq C'\|v\|_{H^1}$$

by the Cauchy–Schwarz inequality, and the fact that $\|\psi^n\|_{H^1}$ is bounded by Lemmas 5.9 and 5.16,

$$\left|\left(\frac{\psi_k^n}{|x - X_K^n|}, v\right)_{L^2}\right| \leq C\big\|\nabla_x\psi^n\big\|_{L^2}\|v\|_{L^2} \leq C'\|v\|_{H^1}$$

by the Cauchy–Schwarz and Hardy's inequality (A.4),

$$\begin{aligned}
&\left|\left(\int \frac{\rho^n(x')}{|x-x'|}\mathrm{d}x'\psi_k^n, v\right)_{L^2}\right| \leq \iint \frac{\rho^n(x)\psi_k^n(x')\overline{v(x')}}{|x-x'|}\mathrm{d}x\,\mathrm{d}x' \\
&\leq \left(\iint \frac{\rho^n(x)\rho^n(x')}{|x-x'|}\mathrm{d}x\,\mathrm{d}x'\right)^{1/2}\left(\iint \frac{\psi_k^n(x)\overline{v(x)}\psi_k^n(x')\overline{v(x')}}{|x-x'|}\mathrm{d}x\,\mathrm{d}x'\right)^{1/2} \\
&\leq C\big\|\psi_k^n\big\|_{L^{12/5}}^2\big\|\psi_k^n v\big\|_{L^{6/5}} \leq C'\big\|\psi_k^n\big\|_{L^{12/5}}^3\|v\|_{L^{12/5}} \leq C''\|v\|_{H^1}
\end{aligned}$$

by [LL01, Theorem 9.8], the Hardy–Littlewood–Sobolev inequality (A.7), Sobolev embedding (Corollary A.8) and Hölder's inequality (A.5), and

$$\begin{aligned}\left|\left(\rho^{n,q-1}\psi_k^n, v\right)_{L^2}\right| &\leq \int \left|\psi_k^n(x)\right|^{2q-1}\overline{v(x)}\mathrm{d}x \leq \left\|\left|\psi^n\right|^{2q-1}\right\|_{L^2}\|v\|_{L^2} \\ &\leq C'\left\|\psi^n\right\|_{H^1}\|v\|_{H^1} \leq C''\|v\|_{H^1}\end{aligned}$$

by the Cauchy–Schwarz inequality and Sobolev embedding in Corollary A.8, as $2q-1 \in [2,6]$.

Eventually, since these terms define the right-hand side of the first equations in (5.3), and $\left(i\dot{\psi}_k^n, v\right)_{L^2}$, which defines the left-hand side, is a linear continuous functional on $H^1$, this also implies the following operator norm is uniformly bounded:

$$\begin{aligned}\left\|\dot{\psi}^n\right\|_{L^\infty((0,T);(W^*)^{N_{\mathrm{el}}})} &\leq \sup_{v\in H^1}\frac{\left|\left(\nabla_x\psi_k^n, \nabla_x v\right)_{L^2}\right|}{\|v\|_{H^1}} + \sup_{v\in H^1}\frac{\left|\left(\dfrac{\psi_k^n}{|x-X_K^n|}, v\right)_{L^2}\right|}{\|v\|_{H^1}} \\ &+ \sup_{v\in H^1}\frac{\left|\left(\displaystyle\int\frac{\rho^n(x')}{|\cdot - x'|}\mathrm{d}x'\psi_k^n, v\right)_{L^2}\right|}{\|v\|_{H^1}} + \sup_{v\in H^1}\frac{\left|\left(\rho^{n,q-1}\psi_k^n, v\right)_{L^2}\right|}{\|v\|_{H^1}} \leq C,\end{aligned}$$

and the second part of the statement follows. □

From the previous Lemma, the following compactness and convergence statements hold, using results by Simon in [Sim86].

**Lemma 5.22.** *Let $T > 0$ be arbitrary, and $\{\psi^n, X^n\}$ be a sequence of solutions of (5.19). The sequence $\{\psi^n\}_{n\in\mathbb{N}}$ is relatively compact in $L^pL^2$ for any $1 \leq p < \infty$, and weakly compact in $L^\infty H^1$. Moreover, the sequence $\{X^n\}$ is compact in $C_b([0,T])$.*

*Together with this, we have the following convergence results:*

$$\begin{aligned}\psi^n &\longrightarrow \psi \qquad \text{in } L^pL^2 \text{ for any } 1 \leq p < \infty, \\ \psi^n &\longrightarrow \psi \qquad \text{in } L^\infty H^1, \\ X^n &\longrightarrow X \qquad \text{in } L^\infty(0,T).\end{aligned}$$

*Proof. Relative compactness in $L^pL^2$ for all $p < \infty$.*
We want to apply the Aubin–Lions–Simon Lemma [Sim86, Cor. 6], which is stated for the Gelfand triple $\widetilde{X} \hookrightarrow \widetilde{B} \hookrightarrow \widetilde{Y}$ of Banach spaces $\widetilde{X}, \widetilde{B}, \widetilde{Y}$, with the embedding $\widetilde{X} \hookrightarrow \widetilde{B}$ compact as follows. Let $1 < \widetilde{q} \leq \infty$. Let the function sequence $\widetilde{F} = \{\widetilde{F}_n\}_{n\in\mathbb{N}}$ be bounded in $L^{\widetilde{q}}([0,T];\widetilde{B}) \cap$

$L^1_{\mathrm{loc}}\big([0,T];\widetilde{X}\big)$ and the function sequence $\partial\widetilde{F}/\partial t = \big\{\dot{\widetilde{F}}_n\big\}_{n\in\mathbb{N}}$ be bounded in $L^1_{\mathrm{loc}}\big([0,T];\widetilde{Y}\big)$. Then, $\widetilde{F}$ is relatively compact in $L^{\widetilde{p}}\big(0,T;\widetilde{B}\big)$ for all $\widetilde{p} < \widetilde{q}$.

We have the Gelfand triple $W^{N_{\mathrm{el}}} \hookrightarrow L^2 \hookrightarrow \big(W^*\big)^{N_{\mathrm{el}}}$, with the first embedding compact by Lemma 5.12. We can apply [Sim86, Cor. 6], by the result of Lemma 5.21, for the Banach spaces $\widetilde{X} = W^{N_{\mathrm{el}}}, \widetilde{B} = L^2, \widetilde{Y} = \big(W^*\big)^{N_{\mathrm{el}}}$, with $q = \infty$, $F_n = \psi^n$. Strong convergence in $L^pL^2$ then follows as a consequence.

*Weak compactness in $L^\infty H^1$.*
Because of our results on the $H^1$ bound in Lemma 5.9 together with the conservation of total energy and electronic charge as shown in Lemma 5.16, we can apply the Banach–Alaoglu theorem in $L^\infty H^1$, where we have the uniform bound

$$\big\|\psi^n\big\|_{L^\infty H^1} = \sup_{t\in(0,T)} \big\|\psi^n(t)\big\|_{H^1} < C$$

such that there is weak-$^*$ convergence of subsequences.

*Compactness in $C_b([0,T])$.*
As a consequence of conservation of energy by Lemma 5.16, the nuclear kinetic energy is bounded:

$$\tfrac{1}{2}\sum_{K=1}^{N_{\mathrm{nuc}}} \big|\dot{X}_K(t)\big|^2 \leq C$$

for all $t$, by which $\dot{X}^n_K$ is bounded in $L^\infty(0,T)$ for all $K$.

By the mean-value theorem on $[0,T]$ and the bound on the kinetic energy, we can see that the assumptions of the Arzelà–Ascoli theorem on $C^0([0,T])$ are satisfied, as we have a sequence of bounded and continuous functions $X^n$, which are bounded in $L^\infty(0,T)$ and equicontinuous. So, this sequence has a uniformly convergent subsequence in the $L^\infty(0,T)$ norm, and $X^n_K$ is compact in $C_{\mathrm{b}}([0,T])$ for all $K$. □

**Remark 5.23.** By the results of [Sim86] in Lemma 5.22, we have the strong convergence $\psi^n \xrightarrow{n\longrightarrow\infty} \psi$ in $L^2L^2$: this gives $\big\|\psi^n(t)\big\|_{L^2} \xrightarrow{n\longrightarrow\infty} \|\psi(t)\|_{L^2}$ for a.e. $t \in [0,T]$. We also know by Lemma 5.16 that for all $n$ we have the charge conservation $\big\|\psi^n(t)\big\|_{L^2} = \big\|\psi^{n0}\big\|_{L^2}$ for a.e. $t \in [0,T]$. With the initial condition $\psi^{n0}$ as in (5.21d), we have $\big\|\psi^{n0}\big\|_{L^2} \xrightarrow{n\longrightarrow\infty}$

$\|\psi^0\|_{L^2}$. As the limit is unique, we also have the charge conservation $\|\psi(t)\|_{L^2} = \|\psi^0\|_{L^2}$ for a.e. $t \in [0,T]$.

Now, we will perform a convergence argument.

**Lemma 5.24.** *Let $\{\psi^n\}_{n\in\mathbb{N}}$ denote a sequence of solutions to (5.19a), and $k = 1,\dots,N_{\mathrm{el}}$. We have the weak convergence*

$$\int \frac{\rho^n(x')}{|\cdot - x'|}\mathrm{d}x'\psi_k^n \xrightarrow{n\longrightarrow\infty} \int \frac{\rho(x')}{|\cdot - x'|}\mathrm{d}x'\psi_k$$

*in $L^\infty L^2$ and almost everywhere.*

*Proof.* Let

$$\xi^n := \int \frac{\rho^n(x')}{|\cdot - x'|}\mathrm{d}x', \qquad \xi := \int \frac{\rho(x')}{|\cdot - x'|}\mathrm{d}x'.$$

We have by Hölder's inequality (A.5)

$$\|\xi^n\psi_k^n\|_{L^2}^2 \le \|\xi^n\|_{L^6}\|\psi_k^n\|_{L^3} \le C\|\nabla_x\xi^n\|_{L^2},$$

as $\|\psi_k^n\|_{L^3}$ is uniformly bounded in $t$ by Lemma 5.21 and Sobolev embedding in Corollary A.8. By Proposition 5.3, it follows that $-\Delta_x\xi^n = \rho^n$. Multiplication by $\xi^n$ and integration by parts then yields

$$\|\nabla_x\xi^n\|_{L^2}^2 = \iint \frac{\rho^n(x)\rho^n(x')}{|x-x'|}\mathrm{d}x\,\mathrm{d}x' \le C\|\psi^n\|_{L^{12/5}}^4 \le C'. \tag{5.34}$$

by the Hardy–Littlewood–Sobolev inequality. Again, $\|\psi_k^n\|_{L^{12/5}}$ is uniformly bounded in $t$ by Lemma 5.21 and Sobolev embedding in Corollary A.8.

Now, we prove the convergence $\xi^n \xrightarrow{n\longrightarrow\infty} \xi$ almost everywhere.

Since by Lemma 5.21, $\|\psi^n\|_{H^1} \le C$ for all $n$, we have up to subsequences $\psi^n \xrightarrow{n\longrightarrow\infty} \psi$ in $L^2_{\mathrm{loc}}$ almost everywhere. By the Hardy–Littlewood–Sobolev inequality (A.7), $\|\nabla_x\xi^n\|_{L^2} \le C$, Now, by [MMV16, Proposition 4.3], $\nabla_x\xi^n \xrightarrow{n\longrightarrow\infty} \nabla_x\xi$ in $L^2$. By the Rellich–Kondrashov theorem [LL01, Theorem 8.9], $\xi^n \xrightarrow{n\longrightarrow\infty} \xi$ in $L^1_{\mathrm{loc}}$, and the result follows. □

**Lemma 5.25.** *Let $\lambda < 0, q \in (1,5/3]$, and $T > 0$ arbitrary. Let $\{\psi^n, X^n\}_{n\in\mathbb{N}}$ denote a sequence of solutions to (5.19), and $(\psi, X)$*

*the corresponding limit. We have for all* $v \in L^2H^1 \cap H^1L^2, Y \in C_c^2\big((0,T);\mathbb{R}^3\big)$

$$
\begin{aligned}
0 &= \big(i\dot{\psi}_k^n, v\big)_{L^2L^2} - \tfrac{1}{2}\big(\nabla_x\psi_k^n, \nabla_x v\big)_{L^2L^2} \\
&\quad + \Bigg(\sum_{K=1}^{N_{\mathrm{nuc}}} \frac{Z_K}{|x - X_K^n|}\psi_k^n - \int \frac{\rho^n(x')}{|\cdot - x'|}\mathrm{d}x'\psi_k^n - \lambda\rho^{n,q-1}\psi_k^n, v\Bigg)_{L^2L^2} \\
&\xrightarrow{n\longrightarrow\infty} -\big(i\psi_k, \dot{v}\big)_{L^2L^2} - \tfrac{1}{2}(\nabla_x\psi_k, \nabla_x v)_{L^2L^2} \\
&\quad + \Bigg(\sum_{K=1}^{N_{\mathrm{nuc}}} \frac{Z_K}{|x - X_K|}\psi_k - \int \frac{\rho(\cdot, x')}{|\cdot - x'|}\mathrm{d}x'\psi_k - \lambda\rho^{q-1}\psi_k, v\Bigg)_{L^2L^2} = 0,
\end{aligned}
\tag{5.35a}
$$

$$
\begin{aligned}
0 &= \int_0^T \ddot{X}_K^n(t)\cdot Y(t)\mathrm{d}t - \int_0^T Z_K \int \rho^n(t,x)\frac{x - X_K^n(t)}{\big|x - X_K^n(t)\big|^3}\mathrm{d}x\cdot Y(t)\mathrm{d}t \\
&\quad - \int_0^T \sum_{L\neq K}^{N_{\mathrm{nuc}}} Z_K Z_L \frac{X_K^n(t) - X_L^n(t)}{\big|X_K^n(t) - X_L^n(t)\big|^3}\cdot Y(t)\mathrm{d}t \\
&\xrightarrow{n\longrightarrow\infty} \int_0^T X_K(t)\cdot\ddot{Y}(t)\mathrm{d}t - \int_0^T Z_K\int \rho(t,x)\frac{x - X_K(t)}{|x - X_K(t)|^3}\mathrm{d}x\cdot Y(t)\mathrm{d}t \\
&\quad - \int_0^T \sum_{L\neq K}^{N_{\mathrm{nuc}}} Z_K Z_L \frac{X_K(t) - X_L(t)}{|X_K(t) - X_L(t)|^3}\cdot Y(t)\mathrm{d}t = 0.
\end{aligned}
\tag{5.35b}
$$

*Proof. Proof of* (5.35a).
We discuss convergence of all separate terms one by one:

- The convergence $\big(i\dot{\psi}_k^n, v\big) \xrightarrow{n\longrightarrow\infty} -(i\psi_k, \dot{v})$ is because of the strong convergence of $\psi^n$ in $L^2L^2$ as shown in Lemma 5.22 and integration by parts.
- The convergence $\big(\nabla_x\psi_k^n, \nabla_x v\big)_{L^2L^2} \xrightarrow{n\longrightarrow\infty} (\nabla_x\psi_k, \nabla_x v)_{L^2L^2}$ holds by weak-* convergence of $\psi^n$ in $L^\infty H^1$.
- The convergence $\left(\frac{\psi_k^n}{|x - X_K^n|}, v\right)_{L^2L^2} \xrightarrow{n\longrightarrow\infty} \left(\frac{\psi_k}{|x - X_K^n|}, v\right)_{L^2L^2}$ holds by weak-* convergence of $\frac{\psi_k^n}{|x - X_K^n|}$ in $L^\infty L^2$.
- The convergence $\left(\int \frac{\rho^n(x')}{|\cdot - x'|}\mathrm{d}x'\psi^n, v\right)_{L^2L^2} \xrightarrow{n\longrightarrow\infty} \left(\int \frac{\rho(x')}{|\cdot - x'|}\mathrm{d}x'\psi, v\right)_{L^2L^2}$ follows from Lemma 5.24.

- The convergence $\left(\rho^{n,q-1}\psi_k^n, v\right)_{L^2L^2} \xrightarrow{n\longrightarrow\infty} \left(\rho^{q-1}\psi_k, v\right)_{L^2L^2}$ holds by weak-* convergence of $\rho^{n,q-1}\psi^n$ in $L^\infty L^2$.

Then, the convergence (5.35a) follows.

*Proof of* (5.35b).
For the convergence of the nuclear equations, we perform the following steps.

First, we bound for all $K = 1, \dots, N_{\text{nuc}}$

$$\begin{aligned}
&\left| \int_0^T \int \rho^n(t,x) \frac{x - X_K^n(t)}{\left|x - X_K^n(t)\right|^3} \mathrm{d}x \cdot Y(t) \mathrm{d}t \right. \\
&\quad \left. - \int_0^T \int \rho(t,x) \frac{x - X_K(t)}{|x - X_K(t)|^3} \mathrm{d}x \cdot Y(t) \mathrm{d}t \right| \\
&\leq \|Y\|_{L^\infty(0,T)} \times \\
&\quad \left[ \int_0^T \underbrace{\left| \int \rho^n(t,x) \frac{x - X_K^n(t)}{\left|x - X_K^n(t)\right|^3} \mathrm{d}x - \int \rho(t,x) \frac{x - X_K^n(t)}{\left|x - X_K^n(t)\right|^3} \mathrm{d}x \right|}_{=:\mathrm{I}(t)} \mathrm{d}t \right. \\
&\quad \left. + \int_0^T \underbrace{\left| \int \rho(t,x) \frac{x - X_K^n(t)}{\left|x - X_K^n(t)\right|^3} \mathrm{d}x - \int \rho(t,x) \frac{x - X_K(t)}{|x - X_K(t)|^3} \mathrm{d}x \right|}_{=:\mathrm{II}(t)} \mathrm{d}t \right].
\end{aligned}$$

We bound

$$\left| \int_0^T \mathrm{I}(t) \mathrm{d}t \right| \leq \int_0^T \int \frac{|\psi^n(t,x)|^2 - |\psi(t,x)|^2}{\left|x - X_K^n(t)\right|^2} \mathrm{d}x \mathrm{d}t \xrightarrow{n\longrightarrow\infty} 0 \tag{5.36}$$

by Conjecture 5.1.

The term $\mathrm{II}(t)$ converges pointwise to 0 for all $t \in [0,T]$ as $n \longrightarrow \infty$. This follows from the continuity of the acceleration functions $A_K^1$ functions in the $\mathbb{R}^3$ topology, which is shown in the proof of Lemma 4.20 (which also holds in the setting of $H^1$), combined with the proof of Lemma 5.17 for the first term in (5.27) of the function $F$.

By (5.30), we have the uniform bound $\left|X_K^n(t) - X_L^n(t)\right| > 2\delta\left(w^0\right)$ on $[0,T]$ for all $n$ and $1 \leq K \neq L \leq N_{\text{nuc}}$. Also, we know that the sequence $\left\{X^n\right\}_{n\in\mathbb{N}}$ is uniformly convergent. This combined gives that

$|X_K - X_L| > 2\delta(w^0)$, and

$$\begin{aligned}
&\left| \int_0^T \frac{X_K^n(t) - X_L^n(t)}{\left|X_K^n(t) - X_L^n(t)\right|^3} \cdot Y(t)\mathrm{d}t - \int_0^T \frac{X_K(t) - X_L(t)}{|X_K(t) - X_L(t)|^3} \cdot Y(t)\mathrm{d}t \right| \\
&\leq T\|Y\|_{L^\infty(0,T)} \operatorname*{ess\,sup}_{t\in[0,T]} \left| \frac{X_K^n(t) - X_L^n(t)}{\left|X_K^n(t) - X_L^n(t)\right|^3} - \frac{X_K(t) - X_L(t)}{|X_K(t) - X_L(t)|^3} \right| \\
&\leq \frac{T\|Y\|_{L^\infty(0,T)}}{4\delta^2} \operatorname*{ess\,sup}_{t\in[0,T]} \left| \left|X_K^n(t) - X_L^n(t)\right| - \left|X_K(t) - X_L(t)\right| \right| \xrightarrow{n\longrightarrow\infty} 0.
\end{aligned}$$

In the convergence of the first term in (5.35b), we perform integration by parts twice.

*Conclusion.*
As stated in Remark 5.19, we know that for all $n \in \mathbb{N}$ the solutions $(\psi^n, X^n)$ to (5.19) also solve (5.3) for all finite linear combinations $v = \sum_{\nu=1}^n c_\nu \phi^\nu \in \operatorname{span}\{\phi^\nu\}_{\nu=1}^n$. Once we pass the limit $n \longrightarrow \infty$, as noted in Lemma 5.14 and Remark 5.15, we can take any element $v \in W$, which can always be expressed as an infinite linear combination $v = \sum_{\nu=1}^\infty c_\nu \phi^\nu \in W$. □

*Proof of Theorem 5.2.* By Lemma 5.18 and Remark 5.19, we know there is a sequence of solutions $\{\psi^n, X^n\}_{n\in\mathbb{N}}$ of the system (5.3) for which the convergence in Lemma 5.22 holds. By the convergence result in Lemma 5.25, the statement in the theorem follows. □

# Chapter 6

# Discussion and outlook

In this chapter, we discuss some of our results in a broader perspective, and shortly address some questions left open to answer in future research.

## 6.1 Discussion of our results

In this thesis, we proved local-in-time existence and uniqueness solutions to our system as presented in (3.5) of time-dependent Kohn–Sham equations coupled with classical nuclear dynamics for parameter values $q \geq 7/2$ and any sign for $\lambda \neq 0$. We also managed to arrive at results aimed at proving global-in-time existence of solutions to this system for parameter values $1 < q \leq 5/3$ and $\lambda < 0$, which include the physically meaningful values for the parameters as presented in the original formulation of the local density approximation (3.1). Note that the existence result we obtained has been formulated for solutions to a weak formulation of the system, as presented in (5.3). The results obtained still leave some questions open.

As discussed in Section 4.2, the particular system we have studied in this thesis, specifically the coupling of time-dependent Kohn–Sham equations with classical nuclear dynamics, has not yet been mathematically investigated. In general, the coupling of electronic dynamics with the time-dependent classical mechanics, thus with moving nuclei, has not yet received much attention by authors.

Note that we formulated our results in a generalisation of the exchange part of the local density approximation: so far, we have put the correlation part of the exchange-correlation term to zero, and only

considered (a generalisation of) the exchange part of the local density approximation. To study explicit formulations of the correlation part in the local-density approximation, like the high- or low-density limit or an interpolation between the two, would be a next step: see also Section 3.1. In addition, other exchange-correlation functionals could be considered.

However, for $1 < q < 3/2$ (so including $q = 4/3$) and $\lambda < 0$ our specific approximation is in line with the mathematical study performed for these extended Kohn–Sham models so far: see e.g. [AC09], where results are formulated on the existence of minimisers for Kohn–Sham models in a time-independent setting, within the framework of approximations as the local density approximation and generalised gradient approximations (GGAs), which also include the gradient of the electronic density as a variable. In this paper, the following conditions on the LDA exchange-correlation functionals have been formulated, under which the results in the article hold.

**Condition 6.1** ([AC09, (25)–(28) in §3])**.** For the integrand in the exchange-correlation energy, that is, $g$ in

$$E_{\mathrm{xc}}[\rho] = \int g(\rho(x))\mathrm{d}x,$$

we state the following. It is a $C^1$ function from $\mathbb{R}^+$ to $\mathbb{R}$, twice differentiable and such that

$$g(0) = 0, \tag{6.1}$$

$$g' \leq 0, \tag{6.2}$$

$$\exists 0 < \beta_- \leq \beta_+ < \frac{2}{3} \quad \text{s.t.} \quad \sup_{\rho\in\mathbb{R}^+} \frac{|g'(\rho)|}{\rho^{\beta_-} + \rho^{\beta_+}} < \infty, \tag{6.3}$$

$$\exists 1 \leq \alpha < \frac{3}{2} \quad \text{s.t.} \quad \limsup_{\rho\downarrow 0} \frac{g(\rho)}{\rho^{\alpha}} < 0. \tag{6.4}$$

Extending this to our time-dependent setting, we can see that our function $g$ in $E_{\mathrm{x}}$ in (3.14), which is

$$g(\rho) = \frac{\lambda}{q}\rho^q,$$

excluding any correlation part, satisfies all these conditions for the range $1 < q < 3/2$ and $\lambda < 0$:

- (6.1) holds for all $\lambda \in \mathbb{R}$ and $q > 0$.

- (6.2) is true for all $\lambda < 0$ and $q > 1$: as $\rho \geq 0$, $g'(\rho) = \lambda\rho^{q-1} \leq 0$.
- (6.3) is satisfied for all $1 < q < 5/3$: as then $0 < q - 1 < 2/3$, we can pick $\beta_- = \beta_+ = q - 1$ and

$$\sup_{\rho\in\mathbb{R}^+} \frac{|g'(\rho)|}{\rho^{\beta_-} + \rho^{\beta_+}} = \frac{|\lambda|}{2} < \infty.$$

- (6.4) is satisfied for all $1 < q < 3/2$ and $\lambda < 0$, as then we can choose $\alpha = q$ and

$$\limsup_{\rho\downarrow 0} \frac{g(\rho)}{\rho^\alpha} = \frac{\lambda}{q} < 0.$$

Moreover, our results can be generalised to other LDA-type nonlinearities $g$, which are homogeneous enough. For example, Theorem 4.1 can be generalised to LDA-type nonlinearities which are sufficiently smooth at the origin $\rho = 0$, and enjoy $H^2$ -Lipschitz estimates similar to those obtained in Section 4.5. This is the case, for instance, for $\lambda_1\rho^{q_1-1} - \lambda_2\rho^{q_2-1}$ with $q_1, q_2 \geq 7/2$ and $\lambda_1, \lambda_2 > 0$, which share a similar structure with nonlinearities involved in various well-known models in quantum mechanics, such as the Thomas-Fermi-Dirac-Von Weizsäcker model [Lie83].

Furthermore, the results in Section 5.2 have a numerical implication. In this section, in the Galerkin approximation method, discretisations of the Kohn–Sham wave functions are constructed, by which we formulate approximated solutions $\psi^n$ of which the elements are written in terms of a truncated sum

$$\psi_k^n(t) = \sum_{\nu=1}^{n} a_{k,\nu}^n(t)\phi^\nu. \tag{6.5}$$

Here, we recall that $a_{k,\nu}^n$ are time-dependent scalar coefficients of class $C^1$ in $\mathbb{C}$, and $\phi^1, \ldots, \phi^n$ are eigenfunctions of the harmonic oscillator on $\mathbb{R}^3$ as in Lemma 5.14, which involve Hermite polynomials. In numerical models in molecular modelling, expansions similar to (6.5) are constructed, using, e.g., the hydrogen wave functions as a basis. If instead we used the basis $\{\phi^\nu\}_{\nu\in\mathbb{N}}$ from (6.5) in numerical applications, there is the potential benefit that one could closely follow the mathematical analysis performed in Chapter 5 for a possible numerical analysis and

structural comparison to other numerical implementations with other choices for the basis. In particular, the estimates on the approximated solution $\psi^n$ could yield numerical as well as theoretical insights. However, when comparing the performances with other basis choices, there is likely the downside of having to work with Cartesian instead of spherical coordinates as with the hydrogen wave functions: this likely renders the implementation to be slow, and a high value of the number of basis functions $n$ would be needed.

## 6.2 Open questions

The main open question is whether we will be able to prove a global existence result in the setting of $H^1$; as of now, we have to rely on Conjecture 5.1. We cannot be sure about whether this conjecture holds. A possible way to circumvent this, and bypass the conjecture, is by a regularisation argument of the following sort. Using the function $G(s) := (\sqrt{s} - \lambda)_+^2$ on $[0, +\infty)$ for $\lambda \geq 0$, we introduce the functions $\varphi_n = G\big(|\psi_n|^2\big) = \alpha(\psi_n)\psi_n$, with $\alpha(\psi_n) = (1 - \lambda/|\psi_n|)_+$. If we bound

$$\lim_{n\to\infty} \int \frac{1}{|x|^2} \big| |\psi_n|^2 - |\psi|^2 \big| \mathrm{d}x \leq \liminf_{n\to\infty} \int \frac{|\varphi_n|^2}{|x|^2} \mathrm{d}x + R(\eta) \leq \frac{C}{\lambda} + R(\eta),$$

for some $\eta = \eta(\lambda) > 0$, with $R(\eta) \to 0$ as $\eta \downarrow 0$, one could formulate the regularised $\eta$-*TDKS equations*, so the TDKS equations with the Coulombic integral replaced by the integral involving $\varphi_n$. If we are able to prove an existence result in the $n \to \infty$ limit without relying on conjecture, we could then subsequently pass the limit $\eta \downarrow 0$ in order to arrive at a similar result for the original system involving the TDKS equations.

Also, it would be interesting to consider whether we can achieve more regularity in the setting of $H^1$ for the weak solutions in Theorem 5.2 under suitable assumptions, such that we would be able to show existence of strong solutions to the original system in the setting of $H^1$ in physically meaningful regions for the parameters $(\lambda, q)$. The uniqueness of these solutions also remains to be proven.

Furthermore, in the setting of $H^2$ we have shown local-in-time well-posedness of solutions in Theorem 4.1 for $q \geq 7/2$. A natural question to consider is what the long-time behaviour of these solutions in the setting of $H^2$ could be.

Recall the article by Cancès & Le Bris we discussed in detail in Section 4.2. We have improved their approach in multiple ways. Firstly, our nuclear feasible region $\mathcal{B}_{\mathrm{nuc}}(\tau)$ is equipped with the $C^0\big([0,\tau];\mathbb{R}^{3N_{\mathrm{nuc}}}\big)$ topology, while in [CB99], the stronger $C^1$ topology is used. We realised the $C^0$ topology is suitable enough and a natural choice to perform the fixed-point argument for the mapping $\mathcal{T}$ in (4.100). The fixed points $X$ of the mapping $\mathcal{T}$ are trajectories which are twice differentiable in the classical sense. Also, we are able to handle the exchange term involving the $q$ parameter, which poses some technical difficulties as in relation to [CB99], which do not treat such a term. In addition, the approach by [CB99] is also further improved using a Grönwall-type argument, namely in Section 4.4, in order to arrive at our own definition of the nuclear feasible region $\mathcal{B}_{\mathrm{nuc}}(\tau)$.

In [CB99], an important difference to note is that they managed to show global existence of solutions in the setting of $H^2$ to a system (4.11) similar to ours, considering the time-dependent Hartree–Fock equations for the electrons. Their proof of global existence [CB99, §3.4] relies on the existence of locally uniform estimates on $|X(t)|$, $\big|\dot{X}(t)\big|$ and $\big\|\psi^{\mathrm{HF}}\big\|_{H^2}$ on any interval $[0,\Theta)$ on which there is local existence and uniqueness. Using the conservation of the total energy and the electric charge, there is a uniform bound $C_0$ such that $\big|\dot{X}(t)\big| + \big\|\nabla\psi^{\mathrm{HF}}(t)\big\|_{L^2} \leq C_0$ on $[0,\Theta)$. By this, $|X(t)|$ is also bounded on $[0,\Theta)$, as well as $\big\|\psi^{\mathrm{HF}}(t)\big\|_{H^1} \leq C_0$. Moreover, for the non-linearity $F\big(\psi^{\mathrm{HF}}\big) = \mathcal{V}_{\mathrm{H}}\big[\rho^{\mathrm{HF}}\big] + \mathcal{V}_{\mathrm{x}}^{\mathrm{HF}}\big[\psi^{\mathrm{HF}}\big]$ on the right-hand side in (4.11), the Lipschitz estimate [CB99, Lemma 5(b)] is of the form

$$\big\|F\big(\psi^{\mathrm{HF}}\big)\big\|_{H^2} \leq C_F\big\|\psi^{\mathrm{HF}}\big\|_{H^1}^2\big\|\psi^{\mathrm{HF}}\big\|_{H^2}$$

for some constant $C_F$. By this, using Duhamel's principle, they get

$$\begin{aligned}\big\|\psi^{\mathrm{HF}}(t)\big\|_{H^2} &\leq \big\|U(t,0)\psi^{\mathrm{HF},0}\big\|_{H^2} + \int_0^t \big\|U(t,t')F\big(\psi^{\mathrm{HF}}(t')\big)\big\|_{H^2}\mathrm{d}t' \\ &\leq B_{\Theta,C_0}\Big(\big\|\psi^{\mathrm{HF},0}\big\|_{H^2} + C_F\big(1+C_0^2\big)\int_0^t \big\|\psi^{\mathrm{HF}}(t')\big\|_{H^2}\mathrm{d}t'\Big).\end{aligned}$$

By applying Grönwall's inequality (A.15), $\big\|\psi^{\mathrm{HF}}(t)\big\|_{H^2} \leq\leq ae^{bt}$ with $a,b$ only depending on the initial data. By this, $\Theta$ can be extended to $+\infty$, and global existence and uniqueness follow.

However, our Lipschitz estimate for the non-linearity $\mathcal{V}_{\mathrm{HX}}[\rho]\psi$ in (4.89) on $H^2$ also includes the $H^2$ norm $\|\psi\|_{H^2}$ itself outside of

$\|\psi - \psi'\|_{C^0([0,\tau];H^2)}$, where this is $\left\|\psi^{\mathrm{HF}}(t)\right\|_{H^1}$ in [CB99]. This is problematic, as this is exactly what we want to bound. In this sense, our local-in-time well-posedness results suggest that there may be a blow-up in finite time possible of the $H^2$ norm of solutions of the system under consideration, as the obstacles for potentially arriving at global-in-time well-posedness results do not seem to be of only a purely mathematical nature.

Since it is unsure whether we can achieve global existence in the setting of $H^2$, it is interesting to explore whether we could achieve global non-existence for certain ranges of exponents $q$ instead of maximal solutions defined for all $t \geq 0$: so, the occurrence of a blow-up at finite time in the norm of the solutions: see [CH98, § 7.6] or [Caz03, § 6.5]. If there were a blow-up occurring at a finite time in the $H^2$ norm, this means that $\|\Delta_x \psi(t)\|_{L^2}$ would blow up in time, or $X$ in some norm on $C^2([0,\tau])$. To this end, we have discussed some identities and bounds for the quantum-classical second moment

$$S(t) = \int |x|^2 |\psi(t,x)|^2 \mathrm{d}x + \sum_{K=1}^{N_{\mathrm{nuc}}} M_K |X_K(t)|^2$$

in Appendix B.3. Then, a blow-up argument could follow from integrating the bound (B.18) in Proposition B.13 twice: this gives a parabola in terms of the time length $T$, which is negative depending on the coefficient in front of the square term, which is an expression involving the initial total energy and the initial condition $\psi^0$. As $S(T)$ is positive by construction and bounded by a possibly negative expression at the same time, for a certain condition on the initial total energy and $\psi^0$, this could lead to a contradiction for $T \longrightarrow \infty$, by which $T$ must be finite, which is equivalent to a finite-time blow-up of the norm $\|\psi\|_{H^2}$ (see e.g. [CH98, Theorem 4.3.4. and Remark 4.3.5.]. However, so far we have only encountered empty conditions, and the study of long-time behaviour of solutions in the setting of $H^2$ is left for future research.

# Appendix A

# Mathematical preliminaries

## A.1 Notation

Throughout the thesis, we make use of the following notations.

### Ordering relation used in inequalities

We write the binary relations $\lesssim$ and $\lesssim_{\alpha,\beta,\ldots}$ on $\mathbb{R}$, with $\alpha, \beta$ parameters, to denote the following types of ordering in inequalities.

Let $A$, $B$ and $\Gamma$ be real quantities. We write

$$A \lesssim B \qquad \text{and} \qquad A \lesssim_{\alpha,\beta,\ldots} B$$

to denote the inequalities

$$|A| \leq CB \qquad \text{resp.} \qquad |A| \leq C_{\alpha,\beta,\ldots} B$$

for some constants $0 < C, C_{\alpha,\beta,\ldots} < \infty$. Note that if

$$A \lesssim_{\alpha} B \lesssim_{\beta} \Gamma, \qquad \text{then} \qquad A \lesssim_{\alpha,\beta} \Gamma.$$

### Further remarks on notation

*Notation of integrals.*
We write

$$\int f(x) \mathrm{d}x$$

with functions $f$ on a known domain $\mathbb{R}^m$ for integration over the whole of $\mathbb{R}^m$.

*Notation of convolutions.*
We denote the *convolution* of two functions $f, g$ by $(f * g)$: that is,

$$(f * g)(x) := \int f(y)g(x-y)\mathrm{d}y.$$

*The direct sum.*
The direct sum $U$ of two vector spaces $U_1, U_2$, written as $U = U_1 + U_2$, is defined as the space of elements $u \in U$ for which there exist unique vectors $u_1 \in U_1, u_2 \in U_2$ such that $u = u_1 + u_2$.

*The space of linear operators.*
The space $\mathcal{L}(B, B')$ denotes the space of all linear operators $A : B \longrightarrow B'$ for Banach spaces $B, B'$. We write $\mathcal{L}(B, B) = \mathcal{L}(B)$.

## A.2 Normed function spaces

In this thesis, we make use of the following normed function spaces. Note that in all inner products, the conjugation is taken on the second argument. Also note that we often use shorthand notation of these spaces without indication of domain or range, so $L^p(\mathbb{R}^3)$, $L^p$, etc., when there is no risk of confusion.

### Lebesgue spaces

The *Lebesgue space* $L^p\big(\mathbb{R}^m; \mathbb{C}^n\big)$ with parameter $p \in [1, \infty]$ contains measurable functions $f : \mathbb{R}^m \longrightarrow \mathbb{C}^n$ for which the following norm is finite:

$$\|f\|_{L^p}^p = \int |f(x)|^p \mathrm{d}x \qquad \text{for } 1 \leq p < \infty, \qquad \|f\|_{L^\infty} = \operatorname{ess\,sup} |f|$$

with the essential supremum

$$\operatorname{ess\,sup} |f| = \inf \big\{ C > 0 \big| |f(x)| \geq C \text{ for a.e. } x \in \mathbb{R}^m \big\}.$$

For $p = 2$, the Lebesgue space forms an inner product space with the inner product

$$(f, g)_{L^2} = \int f(x) \cdot \overline{g(x)} \mathrm{d}x.$$

*The space of locally integrable functions* $L^1_{\mathrm{loc}}(\mathbb{R}^n)$.
If

$$\int_{\varkappa} |f(x)|\mathrm{d}x < \infty$$

on all compact subsets $\varkappa \subset \mathbb{R}^n$, $f$ is called *locally integrable*. The set of locally integrable functions is

$$L^1_{\mathrm{loc}}(\mathbb{R}^n) := \big\{ f : \mathbb{R}^n \longrightarrow \mathbb{C} \text{ measurable } \big| f|_{\varkappa} \in L^1(\varkappa) \text{ for all compact subsets } \varkappa \subset \mathbb{R}^n \big\}.$$

**Sobolev spaces**

The *Sobolev space* $W^{k,p}$ with $k \in \mathbb{N}, p \in [1,\infty]$ contains the functions $f \in L^p$ with $\partial_\alpha f \in L^p$ whenever $|\alpha| \leq k$: that is, all weak derivatives of $f$ up till order $k$ are also in $L^p$. We mostly consider $p = 2$, for which we write $W^{k,2} = H^k$. For these spaces, we are particularly interested in the cases $k = 1, 2$. These spaces we employ with the norms

$$\|f\|^2_{H^1} = \|f\|^2_{L^2} + \||\nabla f|\|^2_{L^2}$$

and

$$\|f\|^2_{H^2} = \|f\|^2_{L^2} + \|\Delta_x f\|^2_{L^2}.$$

*The space* $D^1(\mathbb{R}^n)$.
We define the space

$$D^1(\mathbb{R}^n) := \big\{ f : \mathbb{R}^n \longrightarrow \mathbb{C} \big| f \in L^1_{\mathrm{loc}}(\mathbb{R}^n), \nabla_x f \in L^2(\mathbb{R}^n), \big|\{x \in \mathbb{R}^n \big| f(x) > a\}\big| < \infty \text{ for all } a > 0 \big\}.$$

where $\nabla_x f$ is the distributional derivative of $f$.

*The space* $D^{1,2}(\mathbb{R}^n)$.
We define the space

$$D^{1,2}(\mathbb{R}^n) := \big\{ u \in L^{2^*}(\mathbb{R}^n) \big| \partial_j u \in L^2(\mathbb{R}^n), j \in \{1,2,3\} \big\}, \tag{A.1}$$

with the *Sobolev conjugate* $2^* = 6$.

**Lorentz spaces (Weak Lebesgue spaces)**

The *Lorentz space* $L^{p,r}\big(\mathbb{R}^m;\mathbb{C}^n\big)$, with $1 \le p < \infty$, $1 \le r \le \infty$, contains functions $f : \mathbb{R}^m \longrightarrow \mathbb{C}^n$ for which the following quasi-norm is finite:

$$\|f\|_{L^{p,r}\left(\mathbb{R}^m;\mathbb{C}^n\right)} = \sum_{j=1}^{n} \|f_j\|_{L^{p,r}},$$

$$\|f\|_{L^{p,r}}^r = \int_0^\infty \frac{\left|t^{1/p} f^*(t)\right|^r}{t} \mathrm{d}t \text{ for } 1 \le r < \infty, \ \|f\|_{L^{p,\infty}} = \sup_{t\in\mathbb{R}} \left|t^{1/p} f^*(t)\right|.$$

Here, $f^*$ is the radial decreasing rearrangement

$$f^*(t) = \inf\left\{C > 0 \middle| \left|\left\{x \in \mathbb{R}^m \middle| |f(x)| > C\right\}\right| \le t\right\},$$

For $r = \infty$, these spaces are also called *weak Lebesgue spaces*. We only consider such spaces.

The quasi-norm satisfies the *quasi-triangular inequality*: that is, for all $f, g \in L^{p,r}$

$$\|f + g\|_{L^{p,r}} \le C(\|f\|_{L^{p,r}} + \|g\|_{L^{p,r}}) \tag{A.2}$$

for some $C > 0$.

Furthermore, note that Lorentz spaces can be seen as generalisations of Lebesgue spaces, with $L^{p,p} = L^p$ for all $1 \le p < \infty$.
For more information on Lorentz spaces and rearrangements, see, e.g., [Zie89, §1.8] and [LL01, Chapter 3].

**Other normed spaces**

**The space $L^p([0,T];B)$.**
Let $T > 0$. The Banach space $L^pB = L^p([0,T];B)$ is the space of measurable functions $f : [0,T] \longrightarrow B$ for which the following norms are finite:

$$\|f\|_{L^pB}^p = \int_0^T \|f\|_B^p \mathrm{d}t \text{ for } 1 \le p < \infty, \qquad \|f\|_{L^\infty B} = \operatorname*{ess\,sup}_{t\in(0,T)} \|f(t)\|_B.$$

For $p = 2$ and $B$ an inner product space, the Banach space $L^pB$ forms an inner product space with the inner product

$$(f,g)_{L^2B} = \int_0^T (f,g)_B \mathrm{d}t. \tag{A.3}$$

Similarly, $H^1B$ forms the space

$$H^1B := \{f \in L^2B \big| \partial_t f \in L^2B\}.$$

We use the shorthand notations $L^2L^2$, $L^2H^1$ and $H^1L^2$ for the resulting inner product spaces, using $B = L^2(\mathbb{R}^3;\mathbb{C}^{N_{\text{el}}})$ and $B = H^1(\mathbb{R}^3;\mathbb{C}^{N_{\text{el}}})$.

## A.3 Results on normed spaces

In this thesis, we make use of the following results on the normed spaces we mentioned in Section A.2.

### A.3.1 Results on Lebesgue spaces

The classical $L^p$-Hardy inequality (that is, a multidimensional version of the classic integral inequality extended to $L^p$ spaces) is stated as follows.

**Theorem A.1** (The classical $L^p$-Hardy inequality [VZ00, §2]). *For every $f \in C_0^\infty(\mathbb{R}^n)$ with $n \geq 2, 1 \leq p < n$, we have that $|\cdot|^{-1}f \in L^p(\mathbb{R}^n)$. Moreover,*

$$\| |\cdot|^{-1}f\|_{L^p} \leq \frac{p}{n-p} \| \, |\nabla f| \, \|_{L^p}$$

*with the sharp constant $p/(n-p)$.*

In our context, we use $p = 2, n = 3$, and a translated form.

**Corollary A.2** ([RS19, §2.1]). *for all $f \in C_0^\infty(\mathbb{R}^3)$, $x \in \mathbb{R}^3$, $\big|x-\cdot\big|^{-1}f \in L^2(\mathbb{R}^3)$ with*

$$\big\| |x-\cdot|^{-1}f \big\|_{L^2(\mathbb{R}^3)} \leq 2 \| \, |\nabla f| \, \|_{L^2} \tag{A.4}$$

**Theorem A.3** (Hölder's inequality on Lebesgue spaces [LL01, Theorem 2.3]). *Let $1 \leq p_1, \ldots, p_m \leq \infty$ be such that*

$$\sum_{j=1}^m \frac{1}{p_j} = 1.$$

*Let $f_j$ be in the space $L^{p_j}$ for $j = 1, \ldots, m$. Then, the pointwise product given by $\prod_{j=1}^m f_j$ is in $L^1$, and*

$$\Big| \int \prod_{j=1}^m f_j(x) \mathrm{d}x \Big| \leq \prod_{j=1}^m \|f_j\|_{L^{p_j}}. \tag{A.5}$$

**Remark A.4.** For $m = p_1 = p_2$, this is the *Cauchy-Schwarz inequality* on $L^2$.

**Theorem A.5** (Young's convolution inequality on Lebesgue spaces [LL01, Theorem 4.2])**.** *Let $h := f * g$ denote the convolution of functions*

$$f \in L^{p_1}, g \in L^{p_2}, \text{ with } \frac{1}{p_1} + \frac{1}{p_2} > 1.$$

*Then, $h \in L^r$, with*

$$\frac{1}{p_1} + \frac{1}{p_2} - 1 = \frac{1}{r}.$$

*Furthermore,*

$$\|h\|_{L^r} \leq \|f\|_{L^{p_1}} \|g\|_{L^{p_2}}. \tag{A.6}$$

**Theorem A.6** (Hardy–Littlewood–Sobolev inequality [LL01, Theorem 4.3, p. 106], due to [HL28; HL30; Sob63])**.** *Let $p, r > 1$ and $0 < \lambda < n$ with*

$$\frac{1}{p} + \frac{\lambda}{n} + \frac{1}{r} = 2.$$

*Let $f \in L^p(\mathbb{R}^n)$ and $g \in L^r(\mathbb{R}^n)$. Then, there exists a sharp constant $C(n, \lambda, p)$, independent of $f$ and $h$, such that*

$$\iint \frac{f(x)g(y)}{|x-y|^\lambda} \mathrm{d}x\mathrm{d}y \leq C(n, \lambda, p) \|f\|_{L^p(\mathbb{R}^n)} \|g\|_{L^r(\mathbb{R}^n)}. \tag{A.7}$$

### A.3.2 Results on Sobolev spaces

**Theorem A.7** (Sobolev's inequality for gradients [LL01, Theorem 8.3])**.** *Let $n \geq 3$ and $f \in D^1(\mathbb{R}^n)$. Then $f \in L^p(\mathbb{R}^n)$ with*

$$p = \frac{2n}{n-2}.$$

*Furthermore, the following inequality holds:*

$$\| \, |\nabla_x f| \, \|_{L^2}^2 \geq S_n \|f\|_{L^p}^2. \tag{A.8}$$

*Here, $S_n$ is called the Sobolev constant, with, for $n = 3$, $S_3 = 3(\pi/2)^{4/3}$.*

**Corollary A.8.** *By interpolation, we obtain the continuous Sobolev embedding* $H^1(\mathbb{R}^3)$ *into all Lebesgue spaces* $L^r(\mathbb{R}^3)$ *with* $r \in [2, 6]$.

**Theorem A.9** (Gagliardo–Nirenberg–Sobolev inequality [Eva, Theorem 5.6.1.])**.** *Let* $n \in \mathbb{N}$ *and* $1 \leq p < n$. *Then there exists a constant* $C$, *depending only on* $p$ *and* $n$, *such that*

$$\|f\|_{L^{p^*}(\mathbb{R}^n)} \leq C\|Df\|_{L^p(\mathbb{R}^n)},$$

*for all* $f \in C_c^1$, *with the Sobolev conjugate* $p^*$ *for* $1 \leq p < n$ *given by*

$$\frac{1}{p^*} := \frac{np}{n-p}.$$

**Corollary A.10.** *We have the Sobolev embedding*

$$W^{1,p}(\mathbb{R}^n) \subseteq L^{p^*}(\mathbb{R}^n) \tag{A.9}$$

*for* $1 \leq p < n$.

**Theorem A.11** (A general Sobolev embedding theorem [Eva, Theorem 5.6.6])**.** *Let* $U$ *be a bounded open subset of* $\mathbb{R}^n$, *with a* $C^1$ *boundary. Assume* $f \in W^{k,p}(U)$. *If*

$$k < \frac{n}{p},$$

*then* $f \in L^r(U)$, *where*

$$\frac{1}{r} = \frac{1}{p} - \frac{k}{n}.$$

*We have also the estimate*

$$\|f\|_{L^r(U)} \leq C\|f\|_{W^{k,p}(U)},$$

*the constant* $C$ *depending only on* $k, p, n$ *and* $U$.

**Corollary A.12.** *We have the continuous embedding*

$$W^{k,p}(\mathbb{R}^n) \subseteq W^{\ell,r}(\mathbb{R}^n)$$

*for*

$$\frac{1}{p} - \frac{k}{n} = \frac{1}{r} - \frac{\ell}{n}$$

*where* $k \in \mathbb{N}$, $1 \leq p < \infty$, $k < \ell$, $p < n$ *and* $p < r < \infty$.

### A.3.3 Results on Lorentz spaces

**Theorem A.13** (Young's convolution inequality on Lorentz spaces [Zie89, Theorem 2.10.1]). *Let $h := f * g$ denote the convolution of functions*

$$f \in L^{p_1,q_1}, g \in L^{p_2,q_2}, \text{ with } \frac{1}{p_1} + \frac{1}{p_2} > 1.$$

*Then, $h \in L^{r,s}$, with*

$$\frac{1}{p_1} + \frac{1}{p_2} - 1 = \frac{1}{r},$$

*and $s \geq 1$ any number such that*

$$\frac{1}{q_1} + \frac{1}{q_2} \geq \frac{1}{s}.$$

*Furthermore,*

$$\|h\|_{L^{r,s}} \leq 3r \|f\|_{L^{p_1,q_1}} \|g\|_{L^{p_2,q_2}}. \tag{A.10}$$

**Theorem A.14** (Hölder's inequality on Lorentz spaces [ONe63]). *Let $h := f \cdot g$ denote the (pointwise) product of functions*

$$f \in L^{p_1,q_1}, g \in L^{p_2,q_2}, \text{ with } 1 < p_1, p_2 < \infty, 1 < q_1, q_2 \leq \infty.$$

*Then, $h \in L^{r,s}$, with*

$$\frac{1}{p_1} + \frac{1}{p_2} = \frac{1}{r}, \qquad \frac{1}{q_1} + \frac{1}{q_2} = \frac{1}{s}.$$

*Furthermore,*

$$\|h\|_{L^{r,s}} \lesssim_{p_1,p_2,q_1,q_2} \|f\|_{L^{p_1,q_1}} \|g\|_{L^{p_2,q_2}}. \tag{A.11}$$

**Theorem A.15** (Convolution with a kernel [Zie89, Theorem 2.10.2]). *Let $I_\alpha : \mathbb{R}^n \longrightarrow \mathbb{R}$ denote the kernel*

$$I_\alpha(x) := \|x\|_{\mathbb{R}^n}^{\alpha-n}.$$

*Then*

$$I_\alpha \in L^{\frac{n}{n-\alpha},\infty}. \tag{A.12}$$

*Moreover, if* $f \in L^{p,r}$ *and* $0 < \alpha < n/p$,

$$I_\alpha * f \in L^{r,q}$$

*and*

$$\|I_\alpha * f\|_{L^{r,q}} \leq \|I_\alpha\|_{L^{\frac{n}{n-\alpha},\infty}} \|f\|_{L^{p,q}} \leq C\|f\|_{L^{p,q}}, \tag{A.13}$$

*where*

$$\frac{1}{r} = \frac{1}{p} - \frac{\alpha}{n}.$$

### A.3.4 Other results

**Theorem A.16** (Young's inequality for products)**.** *Let* $a, b \geq 0$ *be non-negative real numbers. Let* $p_1, p_2 > 1$ *be Hölder conjugates: that is,*

$$\frac{1}{p_1} + \frac{1}{p_2} = 1.$$

*Then,*

$$ab \leq \frac{a^{p_1}}{p_1} + \frac{b^{p_2}}{p_2}. \tag{A.14}$$

**Theorem A.17** (Grönwall's inequality)**.** *If* $y$ *satisfies for all* $t \geq t_0$ *the differential and initial inequalities*

$$\begin{aligned} y(t) &\leq ay(t) + b(t), \quad t > t_0, \\ y(t_0) &\leq c, \end{aligned}$$

*then for all* $t \geq t_0$

$$y(t) \leq e^{a(t-t_0)}c + \int_{t_0}^{t} e^{a(t-t')}b(t')\mathrm{d}t'. \tag{A.15}$$

# Appendix B

# Additional results

## B.1 Notes on the variational formulation of the system

Here, we check that the system under consideration (3.5) can be recovered from the evolution equation in the variational formulation (3.13). First, we fix $k \in \{1, \dots, N_{\mathrm{el}}\}$, and take $\widetilde{\psi}_\ell = 0$ for all $\ell \in \{1, \dots, N_{\mathrm{el}}\}$ with $\ell \neq k$. Furthermore, we put $\widetilde{X} = \widetilde{P} = 0$. We write

$$\begin{aligned}
\big|\psi + h\widetilde{\psi}\big|^2 - \rho &= 2h\mathrm{Re}\Big(\psi_k\overline{\widetilde{\psi}_k}\Big) + \mathcal{O}\big(h^2\big),\\
\big|\nabla_x\big(\psi + h\widetilde{\psi}\big)\big|^2 - |\nabla_x\psi|^2 &= 2h\mathrm{Re}\Big(\nabla_x\psi_k \cdot \overline{\nabla_x\widetilde{\psi}_k}\Big) + \mathcal{O}\big(h^2\big),
\end{aligned}$$

and

$$\begin{aligned}
&\big|\psi(x) + h\widetilde{\psi}(x)\big|^2\big|\psi(x') + h\widetilde{\psi}(x')\big|^2 - \rho(x)\rho(x') =\\
&= 2h\Big\{\rho(x)\mathrm{Re}\big[\psi_k(x')\overline{\widetilde{\psi}}_k(x')\big] + \mathrm{Re}\big[\psi_k(x)\overline{\widetilde{\psi}}_k(x)\big]\rho(x')\Big\} + \mathcal{O}\big(h^2\big).
\end{aligned}$$

Furthermore, using the binomial series, we write

$$\begin{aligned}
\big|\psi + h\widetilde{\psi}\big|^{2q} - \rho^q &= \Big\{\rho + \Big[2h\mathrm{Re}\Big(\psi_k\overline{\widetilde{\psi}}_k\Big) + \mathcal{O}\big(h^2\big)\Big]\Big\}^q - \rho^q\\
&= 2hq\rho^{q-1}\mathrm{Re}\Big(\psi_k\overline{\widetilde{\psi}}_k\Big) + \mathcal{O}\big(h^2\big).
\end{aligned}$$

Combining this, we finally obtain, using symmetry in the double integral,

$$\begin{aligned}
&\big\langle D\mathcal{H}(\psi,X,P),(\widetilde{\psi},0,0)\big\rangle = \lim_{h\downarrow 0}\big\{\tfrac{1}{h}\big[\mathcal{H}\big(\psi+h\widetilde{\psi},X,P\big)-\mathcal{H}(\psi,X,P)\big]\big\}\\
&= \mathrm{Re}\Big[\int \nabla_x\psi_k(x)\cdot\overline{\nabla_x\widetilde{\psi}_k(x)}\mathrm{d}x\Big] - 2\sum_{K=1}^{N_{\mathrm{nuc}}} Z_K\mathrm{Re}\Big[\int\frac{\psi_k(x)\overline{\widetilde{\psi}_k(x)}}{|x-X_K|}\mathrm{d}x\Big]\\
&+2\mathrm{Re}\Big[\iint\frac{\rho(x')\psi_k(x)\overline{\widetilde{\psi}_k(x)}}{|x-x'|}\mathrm{d}x\mathrm{d}x'\Big]+2\lambda\mathrm{Re}\Big[\int[\rho(x)]^{q-1}\psi_k(x)\overline{\widetilde{\psi}_k(x)}\mathrm{d}x\Big]\\
&=2\mathrm{Re}\Big[\Big(-\tfrac{1}{2}\Delta_x\psi_k-\sum_{K=1}^{N_{\mathrm{nuc}}}\frac{Z_K}{|\cdot-X_K|}\psi_k+\int\frac{\rho(x')}{|\cdot-x'|}\mathrm{d}x'\psi_k+\lambda\rho^{q-1}\psi_k,\widetilde{\psi}_k\Big)_{L^2(\mathbb{R}^3)}\Big].
\end{aligned}$$

Since in the bilinear form

$$\big[\dot{\psi},\dot{X},\dot{P};\widetilde{\psi},0,0\big]=-2\mathrm{Im}\Big(\big(\dot{\psi}_k,\widetilde{\psi}_k\big)_{L^2(\mathbb{R}^3)}\Big)=2\mathrm{Re}\Big[\big(i\dot{\psi}_k,\widetilde{\psi}_k\big)_{L^2(\mathbb{R}^3)}\Big],$$

we see that the time-dependent Kohn–Sham equations (3.5a) indeed follow from (3.13) by equating the two expressions and using the freedom of choosing $\widetilde{\psi}$ as we imposed.

Then, we fix $K\in\{1,\dots,N_{\mathrm{nuc}}\}$, take $\widetilde{X}_L=0$ for all $L\in\{1,\dots,N_{\mathrm{nuc}}\}$ with $L\neq K$, and put $\widetilde{\psi}=0,\widetilde{P}=0$. We write

$$\begin{aligned}
&\big(|x-X_L|-\big|x-X_L-h\widetilde{X}_L\big|\big)\big(|x-X_L|+\big|x-X_L-h\widetilde{X}_L\big|\big)=\\
&=|x-X_L|^2-\big|x-X_L-h\widetilde{X}_L\big|^2=2h(x-X_L)\cdot\widetilde{X}_L+\mathcal{O}\big(h^2\big).
\end{aligned}$$

Also,

$$\begin{aligned}
&\sum_{L=1}^{N_{\mathrm{nuc}}}Z_L\int\rho(x)\Big[\frac{1}{\big|x-\big(X_L+h\widetilde{X}_L\big)\big|}-\frac{1}{|x-X_L|}\Big]\mathrm{d}x=\\
&=\sum_{L=1}^{N_{\mathrm{nuc}}}Z_L\int\rho(x)\times\\
&\quad\times\frac{\big(|x-X_L|-\big|x-X_L-h\widetilde{X}_L\big|\big)\big(|x-X_L|+\big|x-X_\ell-h\widetilde{X}_L\big|\big)}{\big|x-X_L-h\widetilde{X}_L\big||x-X_L|\big(|x-X_L|+\big|x-X_L-h\widetilde{X}_L\big|\big)}\mathrm{d}x\\
&=2hZ_K\int\rho(x)(x-X_K)\cdot\widetilde{X}_K+\mathcal{O}\big(h^2\big)\times\\
&\quad\times\frac{1}{\big|x-X_K-h\widetilde{X}_K\big|^2|x-X_K|+\big|x-X_K-h\widetilde{X}_K\big|^2|x-X_K|^2}\mathrm{d}x.
\end{aligned}$$

Furthermore, as

$$\begin{aligned}
&\big[|X_L - X_{L'}| - \big|X_L - X_{L'} + h\big(\widetilde{X}_L - \widetilde{X}_{L'}\big)\big|\big)\times \\
&\quad\times \big[|X_L - X_{L'}| + \big|X_L - X_{L'} + h\big(\widetilde{X}_L - \widetilde{X}_{L'}\big)\big|\big) = \\
&= |X_L - X_{L'}|^2 - \big|X_L - X_{L'} + h\big(\widetilde{X}_L - \widetilde{X}_{L'}\big)\big|^2 \\
&= -2h(X_L - X_{L'}) \cdot \big(\widetilde{X}_L - \widetilde{X}_{L'}\big) + \mathcal{O}\big(h^2\big),
\end{aligned}$$

we write

$$\begin{aligned}
&\sum_{\substack{L,L'=1,\\ L\neq L'}}^{N_{\mathrm{nuc}}} Z_L Z_{L'} \left[\frac{1}{\big|\big(X_L + h\widetilde{X}_L\big) - \big(X_{L'} + h\widetilde{X}_{L'}\big)\big|} - \frac{1}{|X_L - X_{L'}|}\right] = \\
&= \sum_{\substack{L,L'=1,\\ L\neq L'}}^{N_{\mathrm{nuc}}} Z_L Z_{L'} \frac{|X_L - X_{L'}| - \big|X_L - X_{L'} + h\big(\widetilde{X}_L - \widetilde{X}_{L'}\big)\big|}{\big|X_L - x_{L'} + h\big(\widetilde{X}_L - \widetilde{X}_{L'}\big)\big||X_L - X_{L'}|}\times \\
&\quad\times \frac{|X_L - X_{L'}| + \big|X_L - X_{L'} + h\big(\widetilde{X}_L - \widetilde{X}_{L'}\big)\big|}{|X_L - X_{L'}| + \big|X_L - X_{L'} + h\big(\widetilde{X}_L - \widetilde{X}_{L'}\big)\big|} \\
&= -2h \sum_{L\neq K}^{N_{\mathrm{nuc}}} Z_K Z_L \big[(X_K - X_L) \cdot \widetilde{X}_K + \mathcal{O}\big(h^2\big)\big]\times \\
&\quad\times \Big[\big|X_K - X_L + h\big(\widetilde{X}_K - \widetilde{X}_L\big)\big|^2 |X_K - K_L| \\
&\qquad + \big|X_K - X_L + h\big(\widetilde{X}_K - \widetilde{X}_L\big)\big||X_K - X_L|^2\Big]^{-1} \\
&\quad - 2h \sum_{L\neq K}^{N_{\mathrm{nuc}}} Z_L Z_K \big[(X_L - X_K) \cdot -\widetilde{X}_K + \mathcal{O}\big(h^2\big)\big]\times \\
&\quad\times \Big[\big|X_L - X_K + h\big(\widetilde{X}_L - \widetilde{X}_K\big)\big|^2 |X_L - X_K| \\
&\qquad + \big|X_L - X_K + h\big(\widetilde{X}_L - \widetilde{X}_K\big)\big||X_L - X_K|^2\Big]^{-1} \\
&= -4h \sum_{L\neq K}^{N_{\mathrm{nuc}}} Z_K Z_L \big[(X_K - X_L \cdot \widetilde{X}_K + \mathcal{O}\big(h^2\big)\big]\times \\
&\quad\times \Big[\big|X_K - X_L + h\big(\widetilde{X}_K - \widetilde{X}_L\big)\big|^2 |X_K - X_L| \\
&\qquad + \big|X_K - X_L + h\big(\widetilde{X}_K - \widetilde{X}_L\big)\big||X_K - X_L|^2\Big]^{-1}.
\end{aligned}$$

Combining this, we obtain

$$\begin{aligned}\big\langle D\mathcal{H}(\psi,X,P),\big(0,\widetilde{X},0\big)\big\rangle &= \lim_{h\downarrow 0}\big\{\tfrac{1}{h}\big[\mathcal{H}\big(\psi,X+h\widetilde{X},P\big)-\mathcal{H}(\psi,X,P)\big]\big\}\\ &= -Z_K\int\rho(x)\frac{(x-X_K)\cdot\widetilde{X}_K}{|x-X_K|^3}\mathrm{d}x-\sum_{L\neq K}^{N_{\mathrm{nuc}}}Z_KZ_L\frac{(X_K-X_L)\cdot\widetilde{X}_K}{|X_K-X_L|^3}.\end{aligned}$$

Since in the bilinear form

$$\big[\dot{\psi},\dot{X},\dot{P};0,\widetilde{X},0\big]=-\dot{P}_K\cdot\widetilde{X}_K,$$

we see that by equating the two expressions and using the freedom of choosing $\widetilde{X}$ as we imposed, we get

$$\dot{P}_K=Z_K\int\rho(x)\frac{x-X_K}{|x-X_K|^3}\mathrm{d}x+\sum_{L\neq K}^{N_{\mathrm{nuc}}}Z_KZ_L\frac{X_K-X_L}{|X_K-X_L|^3}. \tag{B.1}$$

Finally, we fix $K\in\{1,\dots,N_{\mathrm{nuc}}\}$ again, and take $\widetilde{P}_L=0$ for all $L\in\{1,\dots,N_{\mathrm{nuc}}\}$ with $L\neq K$, and put $\widetilde{\psi}=0,\widetilde{X}=0$. We similarly have

$$\begin{aligned}\big\langle D\mathcal{H}(\psi,X,P),\big(0,0,\widetilde{P}\big)\big\rangle &= \lim_{h\downarrow 0}\big\{\tfrac{1}{h}\big[\mathcal{H}\big(\psi,X,P+h\widetilde{P}\big)-\mathcal{H}(\psi,X,P)\big]\big\}\\ &= \frac{P_K\cdot\widetilde{P}_K}{M_K}.\end{aligned}$$

Since in the bilinear form

$$\big[\dot{\psi},\dot{X},\dot{P};0,0,\widetilde{P}\big]=\dot{X}_K\cdot\widetilde{P}_K,$$

we see that by equating the two expressions and using the freedom of choosing $\widetilde{P}$ as we imposed, together with (B.1), we get

$$\begin{aligned}&\dot{X}_K=\frac{P_K}{M_K}\Longrightarrow\ddot{X}_K=\frac{\dot{P}_K}{M_K}=\\ &=\frac{Z_K}{M_K}\bigg[\int\rho(x)\frac{x-X_L}{|x-X_L|^3}\mathrm{d}x+\sum_{L\neq K}^{N_{\mathrm{nuc}}}Z_L\frac{X_K-X_L}{|X_K-X_L|^3}\bigg],\end{aligned}$$

which are indeed the classical-mechanical equations for the nuclei (3.5b).

## B.2 Notes on the energy estimates

In this section, we derive similar bounds for various terms in the total energy as in Section 5.1.2 for the range $(1, 3/2)$ for $q$ and a negative sign for $\lambda$.

First, we bound the term

$$\frac{|\lambda|}{q} \int [\rho(x)]^q \mathrm{d}x.$$

**Lemma B.1** (Coulomb–Sobolev inequality)**.** *Let $\psi \in H^1$. For all $k \in \{1, \dots, N_{\mathrm{el}}\}$, we have*

$$\|\psi_k\|_{L^3}^3 \leq (4\pi)^{-1/2} \|\nabla_x \psi_k\|_{L^2} \left( \iint \frac{|\psi_k(x)|^2 |\psi_k(x')|^2}{|x - x'|} \mathrm{d}x \, \mathrm{d}x' \right)^{1/2}.$$

*Proof.* The following bound is due to P.-L. Lions in [Lio87]; see also [Bel+16; MMV16] for generalisations.

By Proposition 5.3, we know that

$$u_k(x) = \frac{1}{4\pi} \int \frac{|\psi_k(x')|^2}{|x - x'|} \mathrm{d}x' \tag{B.2}$$

is the unique solution in $D^{1,2}$ to the Poisson equation

$$-\Delta_x u = |\psi_k|^2. \tag{B.3}$$

Testing (B.3) with $u_k$ we have

$$\|\nabla_x u_k\|_{L^2}^2 = \frac{1}{4\pi} \iint \frac{|\psi_k(x)|^2 |\psi_k(x')|^2}{|x - x'|} \mathrm{d}x' \mathrm{d}x. \tag{B.4}$$

Testing (B.3) with $|\psi_k| \in H^1$ (see also [LL01, Theorem 9.8 ff., Chapter 10]), we have by the Cauchy–Schwarz inequality

$$\|\psi_k\|_{L^3}^3 = \int \nabla_x u_k(x) \cdot \nabla_x (|\psi_k|)(x) \mathrm{d}x \leq \|\nabla_x u_k\|_{L^2} \|\nabla_x (|\psi_k|)\|_{L^2},$$

from which the result follows, using (B.4) and that $|\nabla_x (|\psi_k|)| \leq |\nabla_x \psi_k|$ holds almost everywhere. □

**Lemma B.2.** *Let $q \in (1, 3/2)$. Let $\psi \in H^1$. For all $\varepsilon > 0$, we have*

$$\frac{|\lambda|}{q}\int [\rho(x)]^q \mathrm{d}x \leq \varepsilon\left[\int |\nabla_x \psi(x)|^2 \mathrm{d}x + \iint \frac{\rho(x)\rho(x')}{|x-x'|}\mathrm{d}x\,\mathrm{d}x'\right] + N_{\mathrm{el}}{}^{\frac{2-q}{3-2q}}\left[\frac{|\lambda|}{(4\pi)^q q}\right]^{\frac{1}{3-2q}}\left(\frac{\varepsilon}{q-1}\right)^{\frac{-2(q-1)}{3-2q}}\|\psi\|_{L^2}^2.$$

*Furthermore, if $q = 3/2$, we have for all $\varepsilon > 0$*

$$\frac{2|\lambda|}{3}\int [\rho(x)]^{3/2}\mathrm{d}x \leq \varepsilon\int |\nabla_x\psi(x)|^2\mathrm{d}x + N_{\mathrm{el}}{}^{-1/2}\frac{3\sqrt{\pi}}{\varepsilon|\lambda|}\iint \frac{\rho(x)\rho(x')}{|x-x'|}\mathrm{d}x\,\mathrm{d}x'.$$

**Remark B.3.** Note that this bound is linear with respect to the electronic charge.

*Proof.* Let $k \in \{1, \dots, N_{\mathrm{el}}\}$. By interpolation, we have

$$\|\psi_k\|_{L^{2q}} \leq \|\psi_k\|_{L^2}^{\beta}\|\psi_k\|_{L^3}^{1-\beta}$$

as long as

$$\frac{1}{2q} = \frac{\beta}{2} + \frac{1-\beta}{3}, \qquad \beta \in (0,1).$$

This gives $\beta = (3-2q)/q$, with $1-\beta = 3(1-q)/q$ for $q \in (1, 3/2)$. By convexity, Lemma B.2, Young's inequality for products (A.14) with exponents $(3-2q)^{-1}, (q-1)^{-1} > 1$ for $q \in (1, 3/2)$, we have for all $\varepsilon > 0$

$$\begin{aligned}
&\frac{|\lambda|}{q}\int [\rho(x)]^q\mathrm{d}x \leq \frac{|\lambda|}{q}N_{\mathrm{el}}{}^{q-1}\sum_{k=1}^{N_{\mathrm{el}}}\|\psi_k\|_{L^{2q}}^{2q}\\
&\leq \sum_{k=1}^{N_{\mathrm{el}}}\frac{|\lambda|N_{\mathrm{el}}{}^{q-1}}{(4\pi)^q q}\left(\frac{\varepsilon}{q-1}\right)^{-2(q-1)}\|\psi_k\|_{L^2}^{2(3-2q)}\left(\frac{\varepsilon}{q-1}\right)^{q-1}\|\nabla_x\psi_k\|_{L^2}^{2(q-1)}\times\\
&\quad\times\left(\frac{\varepsilon}{q-1}\right)^{q-1}\left[\iint\frac{\rho(x)\rho(x')}{|x-x'|}\mathrm{d}x\,\mathrm{d}x'\right]^{q-1}\\
&\leq \varepsilon\left[\int|\nabla_x\psi(x)|^2\mathrm{d}x + \iint\frac{\rho(x)\rho(x')}{|x-x'|}\mathrm{d}x\,\mathrm{d}x'\right]\\
&\quad + N_{\mathrm{el}}\left[\frac{|\lambda|N_{\mathrm{el}}{}^{q-1}}{(4\pi)^q q}\right]^{\frac{1}{3-2q}}\left(\frac{\varepsilon}{q-1}\right)^{\frac{-2(q-1)}{3-2q}}\|\psi\|_{L^2}^2
\end{aligned}$$

Fully analogously, using convexity and Young's inequality for products (A.14), we obtain the bound for the case where $q = 3/2$ by directly applying Lemma B.1. □

Now, we arrive at an estimate on the total kinetic energy.

**Lemma B.4.** *Let $\lambda < 0$, and $q \in (1, 3/2)$. Furthermore, let $T > 0$ arbitrary. Let $X \in C^1([0,T])$ and $\psi \in C^0\big([0,T]; H^1\big)$.*

*For all $0 < \varepsilon < 1/4$, there exists $\mu_\varepsilon < 0$ such that for all $\mu < \mu_\varepsilon$ it holds that for all $t \in [0,T]$*

$$\tfrac{1}{2}\sum_{K=1}^{N_{\mathrm{nuc}}} M_K \big|\dot{X}_K(t)\big|^2 + \tfrac{1}{2}\int |\nabla_x \psi(t,x)|^2 \mathrm{d}x \leq \frac{1}{1-4\varepsilon}\Bigg\{ E[X,\psi](t) + \Bigg\{ \sum_{K=1}^{N_{\mathrm{nuc}}} Z_K + N_{\mathrm{el}}^{\frac{2-q}{3-2q}} \left[\frac{|\lambda|}{(4\pi)^q q}\right]^{\frac{1}{3-2q}} \left(\frac{\varepsilon}{q-1}\right)^{\frac{-2(q-1)}{3-2q}} - \mu N_{\mathrm{nuc}} \Bigg\} \|\psi(t)\|_{L^2}^2 \Bigg\}. \tag{B.5}$$

**Remark B.5.** Note that this bound is linear with respect to the total energy and the electronic charge.

*Proof.* By Lemmas 5.5 and B.2, we bound for all $0 < \varepsilon < 1/4$ the total energy (3.14) by

$$\begin{aligned} E[X,\psi] \geq{}& \tfrac{1}{2}\sum_{K=1}^{N_{\mathrm{nuc}}} M_K \big|\dot{X}_K\big|^2 + (\tfrac{1}{2} - 2\varepsilon)\int |\nabla_x \psi(x)|^2 \mathrm{d}x \\ &+ \tfrac{1}{2}\sum_{\substack{K,L=1,\\ L\neq K}}^{N_{\mathrm{nuc}}} \frac{Z_K Z_L}{|X_K - X_L|} + (\tfrac{1}{2} - \varepsilon)\iint \frac{\rho(x)\rho(x')}{|x-x'|}\mathrm{d}x\,\mathrm{d}x' \\ &+ \Bigg\{ \mu N_{\mathrm{nuc}} - \sum_{K=1}^{N_{\mathrm{nuc}}} Z_K - N_{\mathrm{el}}^{\frac{2-q}{3-2q}} \left[\frac{|\lambda|}{(4\pi)^q q}\right]^{\frac{1}{3-2q}} \left(\frac{\varepsilon}{q-1}\right)^{\frac{-2(q-1)}{3-2q}} \Bigg\} \|\psi\|_{L^2}^2. \end{aligned} \tag{B.6}$$

□

Now, combining the above results, we arrive at a bound on the $H^1$ norm of the Kohn–Sham wave functions $\psi_k$, $k = 1, \ldots, N_{\mathrm{el}}$.

**Lemma B.6.** *Let $\lambda < 0$, and $q \in (1, 3/2)$. Let $T > 0$ arbitrary. Furthermore, let $\psi \in C^0\big([0,T]; H^1\big)$.*

*For all $0 < \varepsilon < 1/4$, there exists $\mu_\varepsilon < 0$ such that for all $\mu < \mu_\varepsilon$ it holds that for all $t \in [0, T]$*

$$\|\psi(t)\|_{H^1}^2 \leq \alpha E[X, \psi](t) + \beta \|\psi(t)\|_{L^2}^2, \tag{B.7}$$

*with*

$$\alpha = \frac{2}{1 - 4\varepsilon},$$
$$\beta = 1 + \frac{2}{1 - 4\varepsilon} \left\{ \sum_{K=1}^{N_{\mathrm{nuc}}} Z_K + N_{\mathrm{el}} \left[ \frac{|\lambda| {N_{\mathrm{el}}}^{q-1}}{(4\pi)^q q} \right]^{\frac{1}{3-2q}} \left( \frac{\varepsilon}{q-1} \right)^{\frac{-2(q-1)}{3-2q}} - \mu N_{\mathrm{nuc}} \right\}.$$

**Remark B.7.** Note that this bound is uniform in time, and independent of the length of the time domain $T$. Further, note that the bound is linear with respect to the total energy and the electronic charge.

*Proof.* Lemma B.4 implies the bound for $\| |\nabla_x \psi(t)| \|_{L^2}^2$ on $[0, T]$, and the result follows. □

## B.3 Notes on the quantum-classical second moment

In this section, we formulate results on the quantum-classical second moment $S$ of the pair $(X, \psi)$ in the setting of $H^2$ for the Kohn–Sham wave function $\psi$, which is defined as

$$S := \int |x|^2 |\psi(x)|^2 \mathrm{d}x + \sum_{K=1}^{N_{\mathrm{nuc}}} M_K |X_K|^2.$$

Here, the second term is the classical analogue of the quantum-mechanical second moment, which is the first term. The following results are partly inspired by results from [CH98, §7.6] on the first term, the quantum part involving $\psi$.

**Lemma B.8** (Second-moment identities)**.** *Let $\psi \in H^1$ be such that $|\cdot|\psi \in L^2$. Then,*

$$\iint \frac{\rho(x)\rho(x')}{|x - x'|} \mathrm{d}x' \mathrm{d}x = 2 \iint \frac{x \cdot (x - x')}{|x - x'|^3} \rho(x')\rho(x) \mathrm{d}x' \mathrm{d}x.$$

*Proof.* The result follows from the observation that $|x-x'|^2 = x\cdot(x-x') + x'\cdot(x'-x)$, symmetry and Fubini's theorem, which we can apply since

$$\iint \left|\frac{x'\cdot(x'-x)}{|x-x'|^3}\rho(x')\rho(x)\right|\mathrm{d}x\mathrm{d}x' \leq \int |x'|\rho(x')\big\||\cdot - x'|^{-1}\psi\big\|_{L^2}^2\mathrm{d}x' \lesssim \||\cdot|\psi\|_{L^2}\|\psi\|_{L^2}\|\nabla_x\psi\|_{L^2}^2.$$

using the Cauchy–Schwarz and Hardy's inequalities (A.4). □

**Lemma B.9.** *Let $T>0$ arbitrary. Let $(\psi, X)$ denote a solution in the space*

$$C^0\big([0,T);H^2\big(\mathbb{R}^3;\mathbb{C}^{N_{\mathrm{el}}}\big)\big)\cap C^1\big([0,T);L^2\big(\mathbb{R}^3;\mathbb{C}^{N_{\mathrm{el}}}\big)\big)\times C^2\big([0,T);\mathbb{R}^{3N_{\mathrm{nuc}}}\big)$$

*to the system (4.1) with $\psi(0)=\psi^0\in H^2$ such that $|\cdot|\psi^0\in L^2$, $X^0\in\mathbb{R}^{3N_{\mathrm{nuc}}}$ with $X_K^0\neq X_L^0$ for $1\leq K\neq L\leq N_{\mathrm{nuc}}$, and $V^0\in\mathbb{R}^{3N_{\mathrm{nuc}}}$.*

*Then, we have*

$$|\cdot|\psi\in C^0\big([0,T);L^2\big),\qquad S\in C^2([0,T)),$$

*with on $[0,T)$*

$$S' = 2\mathrm{Im}\big[(|\cdot|\psi,\partial_r\psi)_{L^2}\big] + 2\sum_{K=1}^{N_{\mathrm{nuc}}} M_K X_K\cdot\dot{X}_K, \tag{B.8}$$

$$\begin{aligned} S'' = {} & 2\int|\nabla_x\psi(x)|^2\mathrm{d}x + 2\sum_{K=1}^{N_{\mathrm{nuc}}} M_K\big|\dot{X}_K\big|^2 - 2\sum_{K=1}^{N_{\mathrm{nuc}}}\int\frac{Z_K}{|x-X_K|}\rho(x)\mathrm{d}x \\ & + \sum_{K=1}^{N_{\mathrm{nuc}}}\sum_{L=1,L\neq K}^{N_{\mathrm{nuc}}}\frac{Z_K Z_L}{|X_K-X_L|} + \iint\frac{\rho(x)\rho(x')}{|x-x'|}\mathrm{d}x'\mathrm{d}x \\ & + \frac{6\lambda(q-1)}{q}\int[\rho(x)]^q\mathrm{d}x, \end{aligned} \tag{B.9}$$

*where $\partial_r$ denotes the radial derivative $\partial_r = x\cdot\nabla_x/|x|$.*

**Remark B.10.** At various places in the proof of Lemma B.9, we use that for functions $g\in L^1(\mathbb{R}^3)$

$$R_n\int_{\partial B_{R_n}} g(x)\mathrm{d}\sigma \longrightarrow 0$$

for some suitable sequence of radii $R_n\longrightarrow\infty$.

*Proof.* Let $I = [0, T']$, $T' < T$. For $\varepsilon > 0$, we define the function $\theta_\varepsilon := \exp\big(-\varepsilon|\cdot|^2\big)$, which is used to regularise the modulus.

*Proof of* (B.8).

On $I$, we define the function

$$f_\varepsilon := \||\cdot|\theta_\varepsilon\psi\|_{L^2}^2, \tag{B.10}$$

with

$$\begin{aligned}
f_\varepsilon' &= 2\mathrm{Re}\big(|\cdot|^2\theta_\varepsilon^2\psi, \dot{\psi}\big)_{L^2} = -2\mathrm{Im}\big(|\cdot|^2\theta_\varepsilon^2\psi, H^{\mathrm{KS}}[X,\rho]\psi\big)_{L^2} \\
&= \mathrm{Im}\big(|\cdot|^2\theta_\varepsilon^2\psi, \Delta_x\psi\big)_{L^2} - 2\mathrm{Im}\bigg[\int |x|^2[\theta_\varepsilon(x)]^2 \times \\
&\quad \times\bigg\{-\sum_{K=1}^{N_{\mathrm{nuc}}}\frac{Z_K}{|x-X_K|} + \int\frac{\rho(x')}{|x-x'|}\mathrm{d}x' + \lambda[\rho(x)]^{q-1}\bigg\}\rho(x)\mathrm{d}x\bigg] \\
&= -\mathrm{Im}\big(|\cdot|^2\theta_\varepsilon^2\Delta_x\psi, \psi\big)_{L^2} \\
&= -\mathrm{Im}\Big[\lim_{R\to\infty}\big\{R^2[\theta_\varepsilon(x)]^2\int_{\partial B_R}\partial_r\psi(x)\cdot\overline{\psi(x)}\mathrm{d}\sigma\big\}\Big] \\
&\qquad + \mathrm{Im}\big(\nabla_x\psi, \nabla_x\big(|\cdot|^2\theta_\varepsilon^2\psi\big)\big)_{L^2} \\
&= \mathrm{Im}\big(\partial_r\big(|\cdot|^2\theta_\varepsilon^2\big)\partial_r\psi, \psi\big)_{L^2} \\
&\quad + \mathrm{Im}\big[\||\cdot|\theta_\varepsilon\nabla_x\psi\|_{L^2}^2\big] + 2\mathrm{Im}\big(\big(1-2\varepsilon|\cdot|^2\big)|\cdot|\theta_\varepsilon^2\partial_r\psi, \psi\big)_{L^2},
\end{aligned}$$

where we use Green's first identity on $B_R$ and Rem. B.10. We have on $I$

$$\begin{aligned}
&f_\varepsilon(t) = \\
&= \big\||\cdot|\theta_\varepsilon\psi^0\big\|_{L^2}^2 + 2\int_0^t \mathrm{Im}\bigg[\int\big(1-2\varepsilon|x|^2\big)|x|[\theta_\varepsilon(x)]^2\partial_r\psi(t',x)\overline{\psi(t',x)}\mathrm{d}x\bigg]\mathrm{d}t' \\
&\leq \big\||\cdot|\psi^0\big\|_{L^2}^2 + C\int_0^t \|\partial_r\psi(t,\cdot)\|_{L^2}\sqrt{f_\varepsilon(t')}\mathrm{d}t' \\
&\leq \big\||\cdot|\psi^0\big\|_{L^2}^2 + \frac{CT'}{2}\|\nabla_x\psi\|_{C^0([0,T'];L^2)}^2 + \frac{C}{2}\int_0^t f_\varepsilon(t')\mathrm{d}t'
\end{aligned}$$

with $C$ independent of $\varepsilon$, using Young's inequality for products (A.14) and that the functions $\theta_\varepsilon$ and $\big(1-2\varepsilon|\cdot|^2\big)\theta_\varepsilon$ are bounded in $x$ and $\varepsilon$. On $I$, we have by Grönwall's inequality (A.15) that $f_\varepsilon \lesssim \exp(CT'/2)$, and,

using Fatou's Lemma, we deduce that $|\cdot|\psi \in C^0\big(I;L^2\big)$. In the limit $\varepsilon \downarrow 0$, we obtain on $I$

$$\||\cdot|\psi(t,\cdot)\|_{L^2}^2 = \big\||\cdot|\psi^0\big\|_{L^2}^2 + 2\int_0^t \mathrm{Im}\big[(|\cdot|\partial_r\psi(t',\cdot),\psi(t',\cdot))_{L^2}\big]\mathrm{d}t'.$$

Since the right-hand side is continuously differentiable, $S \in C^1([0,T))$, and (B.8) holds on $[0,T)$.

*Proof of* (B.9).

For $\varepsilon > 0$, we define on $I$ the function

$$h_\varepsilon := \mathrm{Im}(|\cdot|\theta_\varepsilon\partial_r\psi,\psi)_{L^2}. \tag{B.11}$$

In the following steps, we find expressions for its derivative $h_\varepsilon'$, such that we can perform an argument using the dominated convergence theorem for the limit $\varepsilon \downarrow 0$ in order to arrive at an expression for $S''$.

*Step 1.*
First, we consider $\psi \in C^1\big(I;H^2\big)$. Then, we have on $I$

$$h_\varepsilon' = \mathrm{Im}\big(|\cdot|\theta_\varepsilon\partial_r\dot\psi,\psi\big)_{L^2} - \mathrm{Im}\big(\dot\psi,|\cdot|\theta_\varepsilon\partial_r\psi\big)_{L^2},$$

where

$$\begin{aligned}\big(|\cdot|\theta_\varepsilon\partial_r\dot\psi,\psi\big)_{L^2} = &\int \nabla_x\cdot\big[\theta_\varepsilon(x)\dot\psi(x)\cdot\overline{\psi(x)}x\big]\mathrm{d}x\\ &- \big(\dot\psi,|\cdot|\theta_\varepsilon\partial_r\psi + (3\theta_\varepsilon + |\cdot|\partial_r\theta_\varepsilon)\psi\big)_{L^2}\end{aligned}$$

with

$$\int \nabla_x\cdot\big[\theta_\varepsilon(x)\dot\psi(x)\cdot\overline{\psi(x)}x\big]\mathrm{d}x = \lim_{R\to\infty}\Big\{R\theta_\varepsilon(x)\int_{\partial B_R}\psi(x)\cdot\overline{\dot\psi(x)}\mathrm{d}\sigma\Big\} = 0,$$

using the divergence theorem on $B_R$ together with Rem. B.10. This gives on $I$

$$h_\varepsilon' = -\mathrm{Im}\big(\dot\psi,[2|\cdot|\theta_\varepsilon\partial_r\psi + (3\theta_\varepsilon + |\cdot|\partial_r\theta_\varepsilon)\psi]\big)_{L^2}, \tag{B.12}$$

so $h_\varepsilon \in C^1(I)$. This result is equivalent to

$$\begin{aligned}&h_\varepsilon(t) =\\ &= h_\varepsilon(0) - \int_0^t \mathrm{Im}\big(\dot\psi(t',\cdot),[2|\cdot|\theta_\varepsilon\partial_r\psi(t',\cdot) + (3\theta_\varepsilon + |\cdot|\partial_r\theta_\varepsilon)\psi(t',\cdot)]\big)_{L^2}\mathrm{d}t'\end{aligned}$$

for all $t \in I$. By density, we extend this result to general functions $\psi \in C^0\big(I; H^2\big) \cap C^1\big(I; L^2\big)$.

*Step 2.*
Since $(\psi, X)$ solve (4.1) on $[0, T)$, we have on $I$

$$h'_\varepsilon = \mathrm{Re}\bigg[\Big( -\tfrac{1}{2}\Delta_x\psi + \Big[ -\sum_{K=1}^{N_{\mathrm{nuc}}} \frac{Z_K}{|\cdot - X_K|} + \int \frac{\rho(x')}{|\cdot - x'|}\mathrm{d}x' + \lambda\rho^{q-1}\Big]\psi,$$
$$2|\cdot|\theta_\varepsilon\partial_r\psi + (3\theta_\varepsilon + |\cdot|\partial_r\theta_\varepsilon)\psi\Big)_{L^2}\bigg].$$

*Step 3.*[1] We have on $I$

$$\begin{aligned}
&\mathrm{Re}[(\Delta_x\psi, 2|\cdot|\theta_\varepsilon\partial_r\psi + (3\theta_\varepsilon + |\cdot|\partial_r\theta_\varepsilon)\psi)_{L^2}] = \\
&= \mathrm{Re}\Big[\lim_{R\to\infty}\Big\{2R\theta_\varepsilon(x)\int_{\partial B_R}|\partial_r\psi(x)|^2\mathrm{d}\sigma \\
&\quad + [3\theta_\varepsilon(x) + R\partial_r\theta_\varepsilon(x)]\int_{\partial B_R}\partial_r\psi(x)\cdot\overline{\psi(x)}\mathrm{d}\sigma\Big\}\Big] \\
&\quad - \mathrm{Re}[(\nabla_x\psi, \nabla_x[2\theta_\varepsilon|\cdot|\partial_r\psi + (3\theta_\varepsilon + |\cdot|\partial_r\theta_\varepsilon)\psi])_{L^2}] \\
&= -2\int|x|\partial_r\theta_\varepsilon(x)|\partial_r\psi(x)|^2\mathrm{d}x - 2\mathrm{Re}\big\{(\theta_\varepsilon\nabla_x\psi, \nabla_x[|\cdot|\partial_r\psi])_{L^2}\big\} \\
&\quad - \int\big[4\partial_r\theta_\varepsilon(x) + |x|\partial^2_{rr}\theta_\varepsilon(x)\big]\mathrm{Re}\big[\partial_r\psi(x)\cdot\overline{\psi(x)}\big]\mathrm{d}x \\
&\quad - \int[3\theta_\varepsilon(x) + |x|\partial_r\theta_\varepsilon(x)]|\nabla_x\psi(x)|^2\mathrm{d}x
\end{aligned}$$

[1] In the forthcoming steps, we encounter the integrals

$$\int\theta_\varepsilon(x)x\cdot\int\frac{x-x'}{|x-x'|^3}\rho(x')\rho(x)\mathrm{d}x'\mathrm{d}x, \tag{B.13}$$

$$\int\theta_\varepsilon(x)x\cdot\frac{x-X_K}{|x-X_K|^3}\rho(x)\mathrm{d}x, \qquad k\in\{1,\dots,M\}. \tag{B.14}$$

For all $\varepsilon > 0$, $\theta_\varepsilon$ is uniformly bounded, and the integrands are dominated by an $L^1$ function: to see this, we reason as in the proof of Lemma B.8 for (B.13); for (B.14), we add and subtract $X_K$ in the first entry of the scalar product, and use the Cauchy–Schwarz and Hardy's inequalities.

$$
\begin{aligned}
&= -2 \int \{\theta_\varepsilon(x)|\nabla_x\psi(x)|^2 + |x|\partial_r\theta_\varepsilon(x)|\partial_r\psi(x)|^2\}\mathrm{d}x \\
&\quad - \int \nabla_x \cdot [\theta_\varepsilon(x)|\nabla_x\psi(x)|^2 x]\mathrm{d}x \\
&\quad + \int \big[4\partial_r\theta_\varepsilon(x) + |x|\partial_{rr}^2\theta_\varepsilon(x)\big]\mathrm{Re}\big[\partial_r\psi(x)\cdot\overline{\psi(x)}\big]\mathrm{d}x
\end{aligned}
$$

by Green's first identity on $B_R$ together with Remark B.10, where

$$
\int \nabla_x \cdot \big[\theta_\varepsilon(x)|\nabla_x\psi(x)|^2 x\big]\mathrm{d}x = \lim_{R\to\infty}\Big\{R\theta_\varepsilon(x)\int_{\partial B_R}|\nabla_x\psi(x)|^2\mathrm{d}\sigma\Big\} = 0
$$

by the divergence theorem on $B_R$ together with Remark B.10, and

$$
\begin{aligned}
&\mathrm{Re}\Big[\Big(\Big[-\sum_{K=1}^{N_{\mathrm{nuc}}}\frac{Z_K}{|\cdot - X_K|} + \int\frac{\rho(x')}{|\cdot - x'|}\mathrm{d}x' + \lambda\rho^{q-1}\Big]\psi, 2|\cdot|\theta_\varepsilon\partial_r\psi\Big)_{L^2}\Big] = \\
&= \int |x|\theta_\varepsilon(x)\partial_r\Big\{-\sum_{K=1}^{N_{\mathrm{nuc}}}\frac{Z_K}{|x-X_K|}\rho(x) + \int\frac{\rho(x')}{|x-x'|}\mathrm{d}x'\rho(x) + \frac{\lambda}{q}[\rho(x)]^q\Big\}\mathrm{d}x \\
&+ \int \theta_\varepsilon(x)x\cdot\Big[-\sum_{K=1}^{N_{\mathrm{nuc}}}Z_K\frac{x-X_K}{|x-X_K|^3}\rho(x) + \int\frac{x-x'}{|x-x'|^3}\rho(x')\mathrm{d}x'\rho(x)\Big]\mathrm{d}x,
\end{aligned}
$$

where the first term equals

$$
\begin{aligned}
&\int \nabla_x\cdot\Big\{\theta_\varepsilon(x)\Big[-\sum_{K=1}^{N_{\mathrm{nuc}}}\frac{Z_K}{|\cdot - X_K|}\rho(x) + \int\frac{\rho(x')}{|x-x'|}\mathrm{d}x'\rho(x) + \frac{\lambda}{q}[\rho(x)]^q\Big]x\Big\} - \\
&[3\theta_\varepsilon(x) + |x|\partial_r\theta_\varepsilon(x)]\Big\{-\sum_{K=1}^{N_{\mathrm{nuc}}}\frac{Z_K}{|x-X_K|}\rho(x) + \int\frac{\rho(x')}{|x-x'|}\mathrm{d}x'\rho(x) + \frac{\lambda}{q}[\rho(x)]^q\Big\}\mathrm{d}x,
\end{aligned}
$$

with the first term being

$$
\lim_{R\to\infty}\Big\{R\theta_\varepsilon(x)\int_{\partial B_R}\Big[-\sum_{K=1}^{N_{\mathrm{nuc}}}\frac{Z_K}{|\cdot - X_K|}\rho(x) + \int\frac{\rho(x')}{|x-x'|}\mathrm{d}x'\rho(x) + \frac{\lambda}{q}[\rho(x)]^q\Big]\mathrm{d}\sigma\Big\},
$$

which is 0, using the divergence theorem on $B_R$ together with Rem.

B.10. Altogether, we have on $I$

$$h'_\varepsilon = \int \theta_\varepsilon(x)|\nabla_x\psi(x)|^2\mathrm{d}x + \frac{3\lambda(q-1)}{q}\int \theta_\varepsilon(x)[\rho(x)]^q\mathrm{d}x$$
$$+ \int \theta_\varepsilon(x)x\cdot\Big[-\sum_{K=1}^{N_{\mathrm{nuc}}} Z_K\frac{x-X_K}{|x-X_K|^3} + \int \rho(x')\frac{x-x'}{|x-x'|^3}\mathrm{d}x'\Big]\rho(x)\mathrm{d}x$$
$$+ \int |x|\partial_r\theta_\varepsilon(x)|\partial_r\psi(x)|^2\mathrm{d}x + \frac{\lambda(q-1)}{q}\int |x|\partial_r\theta_\varepsilon(x)[\rho(x)]^q\mathrm{d}x$$
$$+ \tfrac{1}{2}\int \big[4\partial_r\theta_\varepsilon(x) + |x|\partial^2_{rr}\theta_\varepsilon(x)\big]\mathrm{Re}\big[\partial_r\psi(x)\cdot\overline{\psi(x)}\big]\mathrm{d}x.$$

*Step 4.*
Since for all $\varepsilon > 0$ both $\theta_\varepsilon$, $\partial_r\theta_\varepsilon$ $|\cdot|\partial_r\theta_\varepsilon$ and $|\cdot|\partial^2_{rr}\theta_\varepsilon$ are uniformly bounded, we apply the dominated convergence theorem, by which on $I$

$$h'_\varepsilon \xrightarrow{\varepsilon\downarrow 0} \int |\nabla_x\psi(x)|^2\mathrm{d}x + \frac{3\lambda(q-1)}{q}\int [\rho(x)]^q\mathrm{d}x$$
$$- \sum_{K=1}^{N_{\mathrm{nuc}}} Z_K\int x\cdot\frac{x-X_K}{|x-X_K|^3}\rho(x)\mathrm{d}x + \tfrac{1}{2}\iint \frac{\rho(x)\rho(x')}{|x-x'|}\mathrm{d}x'\mathrm{d}x,$$

using Lemma B.8. Similarly, since $|\cdot|\psi \in C^0\big(I;L^2\big)$ (see the proof of (B.8)), we have on $I$

$$h_\varepsilon \xrightarrow{\varepsilon\downarrow 0} \mathrm{Im}(|\cdot|\partial_r\psi,\psi)_{L^2} =: h. \tag{B.15}$$

Note that $h \in C^1(I)$, with $h' = \lim_{\varepsilon\downarrow 0}\{h'_\varepsilon\}$ on $I$. For the nuclear contribution to the result, we observe that on $I$,

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2}\Big(\sum_{K=1}^{N_{\mathrm{nuc}}} M_K|X_K|^2\Big) = 2\sum_{K=1}^{N_{\mathrm{nuc}}} M_K\big|\dot{X}_K\big|^2 + 2\sum_{K=1}^{N_{\mathrm{nuc}}} X_K\cdot A_K[\rho](X).$$

By the identity

$$\sum_{\substack{K,L=1,\\ L\neq K}}^{N_{\mathrm{nuc}}} Z_KZ_LX_K\cdot\frac{X_K-X_L}{|X_K-X_L|^3} =$$
$$= \tfrac{1}{2}\sum_{\substack{K,L=1,\\ L\neq K}}^{N_{\mathrm{nuc}}} Z_KZ_L\frac{X_K\cdot(X_K-X_L)+X_L\cdot(X_L-X_K)}{|X_K-X_L|^3},$$

we have that

$$\frac{\mathrm{d}^2}{\mathrm{d}t^2}\Big(\sum_{K=1}^{N_{\mathrm{nuc}}} M_K|X_K|^2\Big) = 2\sum_{K=1}^{N_{\mathrm{nuc}}} M_K\big|\dot{X}_K\big|^2 + \sum_{K=1}^{N_{\mathrm{nuc}}}\sum_{L=1,L\neq K}^{N_{\mathrm{nuc}}} \frac{Z_K Z_L}{|X_K - X_L|} + 2\sum_{K=1}^{N_{\mathrm{nuc}}} Z_K X_K \cdot \int \frac{x - X_K}{|x - X_K|^3}\rho(x)\mathrm{d}x, \tag{B.16}$$

Using the above results in combination with (B.8), this means that $S \in C^2([0,T))$, and (B.9) holds on $[0,T)$. □

**Proposition B.11** (Second-moment bounds)**.** *Let either*

$$\lambda < 0, q \geq 4/3, \quad \textit{or} \quad \lambda > 0, 1 < q \leq 4/3.$$

*Then, we have on* $[0,T)$

$$S'' \leq 2.E[X,\psi]|_{t=0} + \sum_{K=1}^{N_{\mathrm{nuc}}} M_K\big|\dot{X}_K\big|^2 + \int |\nabla_x \psi(x)|^2 \mathrm{d}x. \tag{B.17}$$

*Proof.* The result follows from (B.9) in Lemma B.9, and the conservation of total energy (3.14), as proven in Lemma 3.3. □

**Remark B.12.** Note that for $q = 4/3$, we have equality in (B.17).

**Proposition B.13.** *Let* $\lambda < 0$*, and* $q \in [4/3, 5/3]$*. For all* $0 < \varepsilon < 1/4$*, there exists* $\mu_\varepsilon < 0$ *such that for all* $\mu < \mu_\varepsilon$ *it holds that on* $[0,T]$

$$S'' \leq 2\frac{1-2\varepsilon}{1-4\varepsilon}.E[X,\psi]|_{t=0} + \frac{2}{1-4\varepsilon}\Big[\Big(\sum_{K=1}^{N_{\mathrm{nuc}}} Z_K - \mu N_{\mathrm{nuc}}\Big)\big\|\psi^0\big\|_{L^2}^2 + N_{\mathrm{el}}{}^{\frac{3}{3q-5}}\left(\frac{\varepsilon q S_3}{|\lambda|}\right)^{\frac{3(q-1)}{3q-5}}\big\|\psi^0\big\|_{L^2}^{\frac{2(3-q)}{5-3q}}\Big]. \tag{B.18}$$

*Proof.* The result follows from Lemma 5.8, energy and charge conservation as proven in Lemma 3.3 and Proposition B.11. □

# Summary

## Well-posedness for time-dependent Kohn–Sham equations coupled with classical nuclear dynamics

In this thesis, we study the initial-value problem associated with a class of time-dependent Kohn–Sham equations coupled with Newtonian nuclear dynamics, which describes the nonadiabatic dynamics of molecular, spin-unpolarised systems.

This type of system is used in the modelling of many dynamical phenomena, like chemical reactions, and other quantum chemistry calculations. For this modelling, computational methods are used to solve the system. These methods can benefit from well-posedness results for the system, as it can validate the nature and behaviour of the numerical solutions and investigate their stability.

The time-dependent Kohn–Sham equations serve as an approximation of the time-dependent Schrödinger equation. They are constructed in the framework of time-dependent density-functional theory, which reduces the electronic evolution to a single-particle description based on the electronic density. This way, the equations are formulated in terms of single-particle wave functions.

The effective potential in the Kohn–Sham description includes an unknown part, the exchange-correlation potential. We study the Kohn–Sham equations in a generalised form of the so-called local density approximation. In this generalisation, we set the correlation term to zero, and investigate a pure-power exchange term with various ranges of exponents as its parameters.

Using a nonadiabatic mixed quantum-classical dynamics method, we couple the time-dependent Kohn–Sham equations, which form a quantum-mechanical description of the electronic evolution, with a

classical-mechanical description of the nuclear dynamics. To this end, we apply the mean-field or Ehrenfest approach, which uses the point-nuclei approximation, by which we treat the nuclei as classical point particles, neglecting their quantum nature. Following this way, we perform a classical limit, in which the nuclei move subject to a single effective potential according to Newtonian dynamics.

The resulting system is a Hamiltonian system, in which the total energy and the electronic charge are conserved quantities over time. For the solutions to the associated initial-value problem to this system in the Sobolev space $H^2$, we are able to show local-in-time existence and uniqueness for a certain range of exponents in the pure-power exchange term. For this proof, we combine Yajima's theory on the construction and properties of propagators for time-dependent, linear Hamiltonians with Duhamel's principle, based on suitable Lipschitz estimates for the non-linear part of the effective Kohn–Sham potential, and apply Schauder's fixed-point theorem in order to arrive at the result.

We are also able to show, under a certain conjecture on convergence, existence of weak solutions in the setting of the Sobolev space $H^1$ for a certain range of exponents in the pure-power exchange term, including the physically meaningful value that appears in the original local density approximation. For this proof, we construct several estimates on terms in the total energy, apply a Galerkin-type method to formulate approximate solutions to a truncated version of the system, and use compactness results in order to perform a convergence argument, under the mentioned conjecture, to prove the existence result.

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# About the author

Wouter Scharpach was born on February 16$^{\text{th}}$, 1996 in Veldhoven, the Netherlands. After finishing high school at the Van Maerlant Lyceum in Eindhoven in 2013, he started studying Industrial and Applied Mathematics at the Eindhoven University of Technology, completing his bachelor's studies in 2016 and his master's studies in 2018. In September 2018, he started as a doctoral student at the Centre for Analysis, Scientific Computing and Applications (CASA) under the supervision of dr. B. Baumeier and dr. C. Mercuri. The results obtained during this doctoral study are presented in this thesis.

From March 2023, Wouter is employed as a patent attorney trainee at DELT$\Delta$P$\Delta$TENTS in Eindhoven.

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