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On the Hartree-Fock dynamics in wave-matrix picture

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Abstract. We introduce the Hamiltonian dynamics with the Hartree-Fock energy in new *wave-matrix* picture. Roughly speaking, the wave matrix is defined as the square root of the density matrix.

The corresponding Hamiltonian equations are equivalent to an operator anticommutation equation. This wave-matrix picture essentially agrees with the density matrix formalism. Its main advantage is that it is Hamiltonian and allows an extension to infinite particle systems like crystals in contrast with the standard HF theory.

Our main result is the existence of the global "reduced" wave-matrix dynamics for finite-particle molecular systems, and the energy and charge conservation laws. For the proof we extend the techniques, based on Hardy's and Sobolev's inequalitites, to the wave-matrix picture.

Contents

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1. Introduction

The first version of the Hartree-Fock method was introduced by Hartree in 1927, and was refined by Fock and Slater about 1930 taking into account the antisymmetry of the fermionic wave functions. The method is widely used in Quantum Chemistry for numerical determination of the ground state of finite particle molecular systems [**28**]. The main idea is the restriction of the test wave functions in the Schrödinger minimization problem to the set of the "Slater determinants". The method is very efficient numerically and the results are in a good agreement with the corresponding experimental data.

The first rigorous results on the existence of the ground state were established by Lieb and Simon [**24**] and by P.-L. Lions [**26**] for finite-particle molecular systems. More general *multiconfiguration* version of the Hartree-Fock theory has been developed in [**19, 18, 21**].

In 2001, the existence of the Hartree-Fock ground state has been established for crystals with space-periodic nuclei arrangements by Catto, Le Bris and P.-L. Lions [**13**]. Next step should be an analysis of the dynamic properties of crystals near the ground state: its stability, dispersion, scattering theory, heat and electric conduction, etc. However, the quantum dynamics of crystals is not rigorously established up to now. For instance, the rigorous quantum theories of Ohm's Law and Fourier's Law are missing [**6, 27**] (see also the Preface [**30**]).

The rigorous time-dependent Hartree-Fock theory has been developed first by Chadam and Glassey [**14**] for the reduced Hartree-Fock equations:

$$i\dot\psi_k(t) = H(t)\psi_k(t),\ k = 1, ..., N;\ \langle\psi_k(t), \psi_l(t)\rangle = \delta_{kl}. \tag{1.1}$$

Here $\psi_k(t) \in L^2 := L^2(\mathbb{R}^3)$ for $t \in \mathbb{R}$, and $H(t) := -\Delta + eV_n(x) + eV_e(x,t)$ where $V_n(x)$ is the potential generated by the (standing) nuclei while $V_e(x,t)$ is the potential generated by moving electrons:

$$V_e(x,t) = \int \frac{\rho(y,t)}{|x-y|}dy,\ \rho(y,t) := e\sum_1^N |\psi_k(y,t)|^2 \le 0, \tag{1.2}$$

where $e < 0$ is the electron charge. The well-posedness in the case of moving nuclei (Hellmann-Feynman nuclei dynamics) has been established by Cancès and Le-Bris [**11**]. The Hartree-Fock equations (1.1) are equivalent to the von Neumann equation

$$i\dot K(t) = [H(t), K(t)] \tag{1.3}$$

for $K(t) := \sum_1^N |\psi_k(t)\rangle\langle\psi_k(t)|$. This equation can be considered for more general *density matrices* $K(t)$ which are nonnegative selfadjoint trace class operators:

$$K^*(t) = K(t) \ge 0,\ K(t) \le 1,\ \mathrm{tr}\, K = N. \tag{1.4}$$

where the condition $K(t) \le 1$ corresponds to the Pauli exclusion principle, and N is the "number of particles". Now $H(t)$ is defined as above with $\rho(y,t) := eK(y,y,t) \le 0$.

Dynamic of density matrices (1.3) was introduced initially by von Neumann and Dirac about 1930 [**17, 29**], and it was used in many cases. For example, in the

superconductivity theory by Bogoliubov [**5**] and Valatin [**32**]. The well-posedness for the von Neumann equation was proved by Bove, Da Prato and Fano [**7, 8**] for a short-range pair-wise interaction potential $w(x-y)$ instead of the Coulomb potential $1/|x-y|$ in (1.2). The case of the Coulomb potential was solved by Chadam [**15**]. Butz and Spohn have applied the von Neumann equation with a source to phase transitions in the fermion/boson production [**9**]. The multiconfiguration dynamics was constructed in [**3**].

However, the dynamical equation (1.3) cannot be extended directly to infinite particle systems like crystals since the corresponding Hamilton generator is infinite: for example, the integral (1.2) diverges if $\rho(\cdot, t)$ is a space-periodic function.

In [**12**], Cances and Stoltz have estabilshed the well-posedness for local perturbations of the periodic ground state density matrix in an infinite crystal in the *random phase approximation*. However, the space-periodic nuclear potential in the equation [**12**, (3)] is fixed that corresponds to the fixed nuclei positions. Thus the back reaction of the electrons onto the nuclei is neglected.

The nonlinear Hartree-Fock dynamics for compact perturbations of the ground state without the random phase approximation was not studied previously, see the discussion in [**20**] and in Introductions of [**10, 12**].

In [**22**], Lewin and Sabin have established the well-posedness for the von Neumann equation (1.3) with density matrices of infinite trace for pair-wise interaction potentials $w \in L^1(\mathbb{R}^3)$. Moreover, the authors prove the asymptotic stability of the ground state in 2D case [**23**]. The integral (1.2) with $w(x-y)$ instead of the Coulomb potential obviously converges for $w \in L^1(\mathbb{R}^3)$ and space-periodic functions $\rho(\cdot, t)$. Let us stress however, that the case of the Coulomb potential in [**22**] is not included.

Thus a selfconsistent theory of the electron-lattice interaction is missing. A natural strategy to remedy the situation would be the renormalization of the Hamilton functional by formal subtraction of infinite ground state energy. However, the Hamilton structure of the von Neumann equation (1.3) is not obvious (though the equations (1.1) are Hamiltonian, see (2.12) below). Hence, the theory requires a suitable Hamilton type modification.

Let us emphasize, that the Hartree-Fock dynamics is not canonically defined since the nonlinear manifold of the Slater determinants is not invariant with respect to the original Schrödinger dynamics. The relevance of the time-dependent Hartree-Fock equations (1.1) is discussed in [**20**, p.340]: "The relation between the time-dependent Hartree-Fock equation and the original Schrödinger equation is mostly unclear (mathematically)". The results [**2**] justify the relation "only for well-prepared initial states (Slater determinants, and slightly more general initial data), and only in the *weak coupling* picture", see [**20**, p.340].

We introduce a modified Hamilton dynamics with the Hamilton functional equal to the Hartree-Fock energy in new 'wave-matrix' picture. The evolution for the corresponding density matrix agrees to some extent with the standard Hartree-Fock equations. Let us stress however, that this evolution is not identical with the Hartree-Fock equations, see Remark 5.4.

The main advantage of this wave-matrix dynamics is that it allows an extension to crystals by the renormalization of the Hamilton functional, as we will show elsewhere.

In present paper we develop the wave-matrix theory for finite particle molecular systems. Our main result is the existence and uniqueness of global solutions for the "reduced" wave-matrix dynamics. All estimates for operator-valued solutions are obtained in the corresponding Sobolev norms of their integral kernels. For the proof we extend the techniques of the Hartree-Fock theory [**11, 14, 15, 24, 26**], based on Hardy's and Sobolev's inequalitites, to the wave-matrices which are operator-valued functions. This extension is our main technical novelty (see Section 6).

We establish the energy and charge conservation as well as all needed properties (1.4) of the corresponding density matrix. We check that for the molecular ground state this wave-matrix picture is equivalent to the standard Hartree-Fock theory. Moreover, we show that the wave-matrix dynamics essentially agrees with the von Neumann equation (1.3).

Our plan is the following. In Sections 2 and 3 we recall the Hartree-Fock theory for the stationary and time-dependent cases. In Section 4 we introduce the wave-matrix Hamilton equations and rewrite it as anticommutation equation. In Section 5 we formulate our main result, and in Section 6 we establish needed technical estimates. In Section 7 we reduce the dynamical equation to the corresponding integral Duhamel-type equation. In Section 8 we construct local solutions, and Section 9 we prove the conservation laws. In Section 10 we obtain a priori bounds and construct global solutions.

In Section 11 we discuss the agreement of the wave-matrix Hamilton equation with the Hartree-Fock density matrix formalism. Finally, in Appendix we calculate variational derivatives of the Hartree-Fock energy in the wave-matrix picture.

2. Hartree-Fock theory of ground state

Let us recall the Hartree-Fock theory for a molecule which consists of M nuclei with charges $|e|Z_j$. Let $x^j \in \mathbb{R}^3$ denote the nuclei locations, and $N = \sum_1^M Z_j$ the number of the electrons. The Schrödinger dynamics for the molecule reads

$$i\dot\Psi(\overline{x},t) = \mathbf{H}\Psi(\overline{x},t) \tag{2.1}$$

$$:= -\sum_1^N \Delta_{x_k}\Psi(\overline{x},t) + e[\sum_1^N V_n(x_k) + V_e(\overline{x})]\Psi(\overline{x},t), \quad \overline{x}\in\mathbb{R}^{3N}.$$

Here $\overline{x} = (x_1, ..., x_N)$, and

$$V_n(x) := \sum_1^M \frac{|e|Z_j}{|x-x_j|},\ V_e(\overline{x}) := \sum_{k<l}\frac{e}{|x_k-x_l|} \tag{2.2}$$

are the potentials generated by the nuclei, and the electrons respectively. The wave function $\Psi(\overline{x},t)$ is antisymmetric in $x_1, ..., x_N$, and the ground state is the state $\Psi(x)$ with the minimal Schrödinger energy

$$E := \min\{\frac{1}{2}\langle\Psi,\mathbf{H}\Psi\rangle :\ \|\Psi\|_{L^2(R^{3N})} = 1\}. \tag{2.3}$$

The Hartree-Fock method takes the minimum over the antisymmetric states of particular form $\Psi(\overline{x}) = \frac{1}{\sqrt{N!}}\det\psi_k(x_l)$ (Slater determinant) with the constraints

$$\langle\psi_k,\psi_l\rangle = \delta_{kl}. \tag{2.4}$$

In this case the Schrödinger energy can be written as the Hartree-Fock functional [**4, 14, 24, 26**]

$$\frac{1}{2}\langle\Psi,\mathbf{H}\Psi\rangle = \mathcal{E}^{HF}(\Psi_N) \quad := \quad \frac{1}{2}\sum_1^N\int|\nabla\psi_k(x)|^2dx+\frac{1}{2}\int V_n(x)\rho(x)dx$$

$$+ \quad \frac{1}{4}\int\frac{\rho(x)\rho(y)}{|x-y|}dxdy-\frac{1}{4}\int\int\frac{|\tau(x,y)|^2}{|x-y|}dxdy. \tag{2.5}$$

Here $\Psi_N := (\psi_1,...,\psi_N)$, while $\rho(x)$ is the electron charge density, and

$$\rho(x) = eK(x,x),\ \tau(x,y) = eK(x,y)\ ,\ K(x,y) := \sum_1^N\psi_k(x)\overline{\psi_k(y)}. \tag{2.6}$$

The *density matrix* K is defined as the operator on the Hilbert space $X := L^2(\mathbb{R}^3)$ with the integral kernel $K(x,y)$. It is the trace class nonnegative selfadjoint operator on X:

$$K^* = K \geq 0,\ K \leq 1,\ \mathrm{tr}\,K = N. \tag{2.7}$$

We keep throughout identical notations for operators and their integral kernels. The energy $\mathcal{E}^{HF}(\Psi_N)$ can be expressed in the density matrix (2.6) as

$$\mathcal{E}^{HF}(K) \quad = \quad -\frac{1}{2}\,\mathrm{tr}\,\Delta K+\frac{1}{2}\int V_n(x)\rho(x)dx$$

$$+\frac{1}{4}\int\frac{\rho(x)\rho(y)}{|x-y|}dxdy-\frac{1}{4}\int\int\frac{|\tau(x,y)|^2}{|x-y|}dxdy. \tag{2.8}$$

Let us denote by $\mathcal{S}(N)$ the set of all $\Psi_N = (\psi_1,...,\psi_N) \in \oplus_1^N X$ satisfying the constraints (2.4). Then the Hatree-Fock approximation for the ground state energy (2.3) reads

$$E^{HF} := \min\{\mathcal{E}^{HF}(\Psi_N):\ \Psi_N \in \mathcal{S}(N)\} \geq E. \tag{2.9}$$

Further, the density matrix $K = K(\Psi_N) = \sum|\psi_k\rangle\langle\psi_k|$ is invariant with respect to the unitary transformations

$$\Psi_N = (\psi_k : k = 1,...,N) \mapsto \Phi_N = (\phi_k = \sum U_{kl}\psi_l : k = 1,...,N),\ (U_{kl}) \in U(N). \tag{2.10}$$

Respectively, the Hartree-Fock energy $\mathcal{E}^{HF}$ also is $U(N)$-invariant functional.

The Hartree-Fock theory is widely used in quantum chemistry [**28**]. Namely, the minimization of the energy (2.5) under the constraints (2.4) provides a good approximation to the molecular ground state energy (2.3). The crucial advantage of this minimization problem is that it concerns N functions of 3 variables while the original Schrödinger problem (2.3) concerns one function of $3N$ variables. However, the problem with $3N$ variables is numerically unrealistic even for $N = 10$ (as for the water molecule H_2O) since the function of 30 variables with 20 points in each variable requires at least 20^{30} "cells" in memory, while N functions of 3 variable require 10×20^3 cells.

The Lagrange multipliers method leads to the variational equations

$$D_{\overline{\psi}_k}\mathcal{E}^{HF}(\Psi_N) = \sum_{l=1}^N\lambda_{kl}\psi_l,\ k = 1,...,N. \tag{2.11}$$

Here $D_{\overline{\psi_k(x)}} := D_{p_k(x)} + iD_{q_k(x)}$ where $p_k(x) = \operatorname{Re}\psi_k(x)$ and $q_k(x) = \operatorname{Im}\psi_k(x)$. Furthermore, the calculation gives that

$$D_{\overline{\psi_k}}\,\mathcal{E}^{HF}(\Psi_N) = H\psi_k, \tag{2.12}$$

where $H = H(\Psi_N)$ is the symmetric operator in X with the domain $\mathcal{D} := C_0^\infty(\mathbb{R}^3)$,

$$H(\Phi_N) = -\Delta + eV_n(x) + eV_e(x) + e\mathcal{T}. \tag{2.13}$$

Here the potential generated by the electrons, $V_e(x)$, and the operator $\mathcal{T}$ are given by

$$V_e(x) = \int \frac{\rho(y)}{|x-y|}dy,\ \mathcal{T}\psi(x) = -\int \frac{\tau(x,y)}{|x-y|}\psi(y)dy. \tag{2.14}$$

Now (2.11) reads as [**26**, (12)]

$$H(\Psi_N)\psi_k = \sum_{l=1}^{N} \lambda_{kl}\psi_l,\ k = 1, ..., N. \tag{2.15}$$

Finally, the matrix $\Lambda = (\lambda_{kl})$ is Hermitian since $H(\Psi_N)$ is the symmetric operator. Hence, applying to the both sides of (2.15) the matrix U, which diagonalize (λ_{kl}), we obtain [**26**, (13)]

$$H(\Phi_N)\phi_k = \varepsilon_k\phi_k,\ k = 1, ..., N \tag{2.16}$$

since $H(\Psi_N)$ is invariant with respect to the unitary transformations (2.10).

The first results on existence of the ground state for finite-particle molecular systems were established by Lieb and Simon [**24**] and P.-L. Lions [**26**]. By Lieb's result [**25**] (see also [**1**]), the minimization of the energy $\mathcal{E}^{HF}$ over the Slater-type density matrices is equivalent to its minimization over general density matrices with integral kernel

$$K(x,y) = \sum \lambda_n u_n(x)\overline{u_n(y)}\ ,\ \langle u_k, u_l\rangle = \delta_{kl}\ ,\ 0 \le \lambda_n \le 1\ ,\ \sum \lambda_n = N. \tag{2.17}$$

In these notations the result [**25**] means that

$$E^{HF} = \min\{\mathcal{E}^{HF}(K) :\ K^* = K,\ 0 \le K \le 1,\ \operatorname{tr} K = N\}. \tag{2.18}$$

3. Hartree-Fock dynamics

The structure of the stationary equations (2.16) suggests the dynamical Hartree-Fock equations considered in [**11, 14**]:

$$i\dot{\psi}_k(x,t) = H(t)\psi_k(\cdot,t),\ k = 1, ..., N. \tag{3.1}$$

Here $H(t) = H(\Psi(t))$ is the operator of type (2.13):

$$H(t) := -\Delta + eV_n(x) + eV_e(x,t) + e\mathcal{T}(t) \tag{3.2}$$

with the potential $V_e(x,t)$ and the operator $\mathcal{T}(t)$ defined similarly to (2.14):

$$V_e(x,t) = \int \frac{\rho(y,t)}{|x-y|}dy,\ \mathcal{T}(t)\psi(x) = -\int \frac{\tau(x,y,t)}{|x-y|}\psi(y)dy, \tag{3.3}$$

where $\rho(y,t)$ and $\tau(x,y,t)$ correspond to the density matrix

$$K(x,y,t) := \sum_{1}^{N} \psi_k(x,t)\overline{\psi_k(y,t)}.$$

The Hatree-Fock dynamics (3.1) can be expressed via this density matrix as the von Neumann equation

$$i\dot{K}(t) = [H(t), K(t)], \tag{3.4}$$

where $K(t)$ is the operator with the integral kernel $K(x, y, t)$, and $H(t)$ is the corresponding operator (3.2).

In [**14**] the global solutions were constructed for the reduced Hartree-Fock equations (3.1) (i.e., with the operator (3.2) without the last term). In [**15**] the result has been extended to the equation (3.4) with general density matrices (2.17). In [**11**] the existence of global solutions has been proved for equation (3.1) coupled to the Newton equations for the nuclei.

4. Wave-matrix picture

The dynamic equations (3.1) are Hamiltonian by (2.12). On the other hand, the Hamilton structure of general equation (3.4) is not obvious.

Let us recall, that the Hartree-Fock dynamics is not canonically defined since the nonlinear manifold of the Slater determinants is not invariant with respect to the original Schrödinger dynamics (2.1). We suggest a modified Hamiltonian dynamics for general density matrices in a novel "wave-matrix" representation $K = ww^*$, or equivalently

$$K(x, y) = \int w(x, z)w^*(z, y)dz = \int w(x, z)\overline{w(y, z)}dz\ , \tag{4.1}$$

where $w(x, z)$ is the integral kernel of the operator w. For example, we can take $w := K^{1/2}$ for any density matrix (2.17). The representation is suggested by the eigenfunction expansions (2.6) and (2.17). Obviously, K is a trace class selfadjoint operator for any Hilbert-Schmidt operator w.

Below we introduce the corresponding dynamics for the wave matrices $w(x, y, t)$. We will show that this dynamics provides

i) The same ground state energy as constructed in [**24, 25, 26**].

ii) All properties (2.7) for the density matrix (4.1) at any time $t \in \mathbb{R}$ once they hold at $t = 0$.

iii) The evolution for the corresponding density matrix $K(t) = w(t)w^*(t)$ which agrees to some extent with equation (3.4), see Remark 5.4.

Let us note that we do not fix the number of particles which is equal to $\operatorname{tr} K$ and coincides with the Hilbert-Schmidt norm of w. We will show that this number is conserved along the wave-matrix dynamics.

First, we generalize the definition (2.5) of the Hartree-Fock energy for the wave-matrices:

$$\begin{aligned}\tilde{\mathcal{E}}^{HF}(w) \quad := \quad & \frac{1}{4}\int\int[|\nabla_x w(x, y)|^2 + |\nabla_y w(x, y)|^2]dxdy \\ & + \frac{e}{4}\int\int[V_n(x) + V_n(y)]|w(x, y)|^2 dxdy \\ & + \frac{1}{4}\int\int\frac{\tilde{\rho}(x)\tilde{\rho}(y)}{|x - y|}dxdy - \frac{1}{4}\int\int\frac{|\tilde{\tau}(x, y)|^2}{|x - y|}dxdy.\end{aligned} \tag{4.2}$$

Here $\tilde\rho(x)$ and $\tilde\tau(x,y)$ are defined similarly to (2.6):

$$\begin{aligned}\tilde\rho(x) &= e\tilde K(x,x),\ \tilde\tau(x,y)=e\tilde K(x,y),\\ \tilde K(x,y) &:= \frac12\int[w(x,z)\overline{w(y,z)}+\overline{w(z,x)}w(z,y)]dz.\end{aligned}\tag{4.3}$$

In other words, $\tilde K(x,y)$ is the integral kernel of the symmetric nonnegative operator

$$\tilde K=\frac12\{w,w^*\}=\frac12[ww^*+w^*w]\tag{4.4}$$

The energy (4.2) can be expressed in the density matrix $\tilde K$ similarly to (2.8):

$$\tilde{\mathcal{E}}^{HF}(w)=\mathcal{E}^{HF}(\tilde K).\tag{4.5}$$

Note that the "Slater-type" density matrices $K=\sum_1^N|\psi_k\rangle\langle\psi_k|$ admit representation (4.1) with $w=K$ since $K^*=K$ and $K^2=K$ due to the constraints (2.4). Hence, in this case

$$\tilde K=w=K,\ \tilde\rho=\rho,\ \tilde\tau=\tau.\tag{4.6}$$

In this "wave-matrix" representation we accept $\tilde{\mathcal{E}}^{HF}(w)$ as the Hamilton functional. Respectively, we define the Hamilton wave-matrix dynamics formally by

$$i\dot w(x,y,t)=2D_{\overline w(x,y)}\tilde{\mathcal{E}}^{HF}(w(\cdot,t))=-[\Delta_x+\Delta_y]w(x,y,t)+...\tag{4.7}$$

Here $D_{\overline w(x,y)}:=D_{w_1(x,y)}+iD_{w_2(x,y)}$ where $w_1(x,y)=\operatorname{Re}w(x,y)$ and $w_2(x,y)=\operatorname{Im}w(x,y)$. We change the "standard" Hamilton structure introducing the prefactor 2, to reconcile the dynamics with the von Neumann equation (3.4) as we will show later.

Let us denote by $\tilde H(t)$ the operator (3.2) with the potential $V_e(x,t)$ and the operator $\mathcal{T}(t)$ changed to the corresponding $\tilde V_e(x,t)$ and $\tilde{\mathcal{T}}(t)$ which are defined similarly to (3.3):

$$\tilde H(t):=-\Delta+eV_n(x)+e\tilde V_e(x,t)+e\tilde{\mathcal{T}}(t),\tag{4.8}$$

$$\tilde V_e(x,t)=\int\frac{\tilde\rho(y,t)}{|x-y|}dy,\ \tilde{\mathcal{T}}(t)\psi(x)=-\int\frac{\tilde\tau(x,y,t)}{|x-y|}\psi(y)dy.\tag{4.9}$$

Formally calculating the variational derivative in (4.7), we obtain

$$i\dot w(t)=\{\tilde H(t),w(t)\}:=\tilde H(t)w(t)+w(t)\tilde H(t).\tag{4.10}$$

We justify this calculation in Lemma 5.2 for the *reduced* equation (4.7).

5. Wave-matrix dynamics

We will prove the existence and uniqueness of global solutions to the reduced equation (4.10) when the operator $\tilde H(t)$ is defined by (4.8) without $\tilde{\mathcal{T}}(t)$. In other words, from now on,

$$\tilde H(t):=H_0+\tilde V(t),\ H_0:=-\Delta+eV_n(x)\ \tilde V(t):=e\tilde V_e(x,t).\tag{5.1}$$

Respectively, the Hamiltonian $\mathcal{E}^{HF}(w)$ now is changed to the reduced Hartree-Fock energy

$$\tilde{\mathcal{E}}^{RHF}(w)=\frac12\operatorname{tr}[H_0\tilde K(t)]+\frac14\int\frac{\tilde\rho(x)\tilde\rho(y)}{|x-y|}dxdy,\tag{5.2}$$

and the corresponding dynamic equation (4.7) formally reads

$$i\dot{w}(t) = 2D_{\overline{w}}\tilde{\mathcal{E}}^{RHF}(w(\cdot,t)),\ t\in\mathbb{R}. \tag{5.3}$$

To formulate our main results we need the following definition. Let us denote by $\mathcal{L}^2$ the Hilbert space of the Hilbert-Schmidt operators in L^2.

Definition 5.1. $\mathbf{H}^s$ with $s = 0, 1, ...$ denotes the space of operators $w \in \mathcal{L}^2$ endowed with the finite norm

$$\|w\|^2_{\mathbf{H}^s} = \sum_{|\alpha|\le s}\int |\partial^\alpha_{(x,y)}w(x,y)|^2dxdy, \tag{5.4}$$

where $w(x, y)$ denotes the integral kernels of w.

Equivalently, $\partial^\alpha_x w \in \mathcal{L}^2$ and $w\partial^\alpha_x \in \mathcal{L}^2$ for $|\alpha| \le s$. In particular, $\mathbf{H}^0 = \mathcal{L}^2$.

We will construct strong solutions $w(\cdot) \in X := C^1_s(\mathbb{R}, \mathbf{H}^0) \cap C(\mathbb{R}, \mathbf{H}^2)$, where C^1_s denotes the strongly differentiable operator functions, while $C(\mathbb{R}, \mathbf{H}^2)$ denotes the space of continuous operator functions in the norm $\mathbf{H}^2$. In this case the equation (5.3) can be written as

$$i\dot{w}(t) = \{\tilde{H}(t), w(t)\},\ t\in\mathbb{R} \tag{5.5}$$

by the following lemma.

Lemma 5.2. *The Hamilton functional $\tilde{\mathcal{E}}^{RHF}$ is Gâteaux differentiable on the space $\mathbf{H}^2$, and*

$$2D_{\overline{w}}\tilde{\mathcal{E}}^{RHF}(w) = \{\tilde{H}, w\} \in \mathbf{H}^0,\ w\in\mathbf{H}^2, \tag{5.6}$$

where $\tilde{H} = H_0 + e\tilde{V}_e(x)$ and $\tilde{V}_e(x) := \int \frac{\tilde{\rho}(y)}{|x-y|}dy$.

We prove this lemma in Appendix. Our main result is the following theorem.

Theorem 5.3. *For any initial state $w(0) \in \mathbf{H}^2$ there exists the unique strong solution $w(\cdot) \in X$ to (5.5).*

For the proof we follow the standard scheme: first we prove some technical estimates and construct the local solutions; afterwords, we prove a priori estimates which give the global strong solutions.

In conclusion, let us differentiate the density matrix $K(t) := w(t)w^*(t)$ for a solution $w(\cdot) \in X$ to (5.5). Taking the adjoint to (5.5), we get $-i\dot{w}^*(t) = w^*(t)\tilde{H}(t) + \tilde{H}(t)w^*(t)$, and hence,

$$i\dot{K}(t) = i[\dot{w}(t)w^*(t)+w(t)\dot{w}^*(t)] = [\tilde{H}w+w\tilde{H}]w^*-w[w^*\tilde{H}+\tilde{H}w^*] = [\tilde{H}(t), K(t)]. \tag{5.7}$$

Remark 5.4. Equation (5.5) for the wave matrix $w(t)$ agrees with the von Neumann equation (3.4) for $K(t) := w(t)w^*(t)$ at such times t that $w(t)$ is the Slater-type density matrix. Namely, $\tilde{H}(t) = H(t)$ for these times by (4.6), and hence (5.7) coincides with (3.4) for these times. Let us stress however, that the evolution of $K(t) = w(t)w^*(t)$ is not identical to (3.4).

6. Basic estimates

We extend basic estimates [**11**] to the wave-matrix formalism. First let us obtain estimates for the potential $\tilde V_e$ defined in (4.9):

$$\tilde V_e(x)=\int\frac{\tilde\rho(y)}{|x-y|}dy=\frac12\int\frac{\int[w(y,z)\overline{w}(y,z)+\overline{w}(z,y)w(z,y)]dz}{|x-y|}dy. \tag{6.1}$$

LEMMA 6.1. *Let $w\in\mathbf{H}^1$. Then*

$$\sup_{x\in\mathbb{R}^3}|\tilde V_e(x)|\le C\|w\|_{\mathbf{H}^0}\|w\|_{\mathbf{H}^1}. \tag{6.2}$$

PROOF. Let us denote the integrand

$$\tilde V_e(x,z)=\frac12\int\frac{w(y,z)\overline{w}(y,z)+\overline{w}(z,y)w(z,y)}{|x-y|}dy. \tag{6.3}$$

Applying the Cauchy-Schwarz and Hardy inequality [**16**, p.446], we obtain

$$|\tilde V_e(x,z)|\le C(\|w(\cdot,z)\|\cdot\|\nabla_1 w(\cdot,z)\|+\|w(z,\cdot)\|\cdot\|\nabla_2 w(z,\cdot)\|), \tag{6.4}$$

where $\|\cdot\|$ denotes the norm in L^2, and ∇_1, ∇_2 are obvious notations. Now the integration over $z\in\mathbb{R}^3$ gives (6.2) by the Cauchy-Schwarz inequality. □

This lemma implies that the anticommutator

$$F(w)=\{\tilde V_e,w\} \tag{6.5}$$

is the Hilbert-Schmidt operator on L^2 for $w\in\mathbf{H}^1$. The anticommutator $\{\Delta,w\}$ is the Hilbert-Schmidt operator for $w\in\mathbf{H}^2$. Finally, $\{V_n,w\}$ is the Hilbert-Schmidt operator for $w\in\mathbf{H}^1$ by the Hardy inequality. As the result, the right hand side of (5.5) is well defined Hilbert-Schmidt operator for $w(\cdot)\in X$.

Further we need the local Lipschitz continuity for the anticommutator (6.5). Next two lemmas extend Lemma 5 of [**11**] to the wave-matrix formalism. The first lemma concerns the Lipschitz continuity in $\mathbf{H}^0$, and the second one - in $\mathbf{H}^2$.

LEMMA 6.2. (cf. Lemma 5 (a) of [**11**]) *For $w,w'\in H^1$*

$$\|F(w)-F(w')\|_{\mathbf{H}^0}\le C(\|w\|^2_{\mathbf{H}^1}+\|w'\|^2_{\mathbf{H}^1})\|w-w'\|_{\mathbf{H}^0}. \tag{6.6}$$

PROOF. It suffices to prove (6.6) for one term

$$F_1(w)=w\int\frac{\int w(y,z)\overline{w}(y,z)dz}{|x-y|}dy \tag{6.7}$$

since the proof for the other term is similar. Obviously,

$$\begin{aligned}F_1(w)-F_1(w') &= (w-w')\int\frac{\int w(y,z)\overline{w}(y,z)dz}{|x-y|}dy\\ &+w'\int\frac{\int[w(y,z)\overline{w}(y,z)-w'(y,z)\overline{w}'(y,z)]dz}{|x-y|}dy.\end{aligned} \tag{6.8}$$

The first term on the right hand side admits the bound (6.6) by previous lemma. For the second term we estimate the "integrand" as in (6.4):

$$\begin{aligned} I(x,z) &= \int \frac{w(y,z)\overline{w}(y,z) - w'(y,z)\overline{w}'(y,z)}{|x-y|}dy \\ &= \int \frac{w(y,z)\overline{w}(y,z) - w'(y,z)\overline{w}(y,z) + w'(y,z)\overline{w}(y,z) - w'(y,z)\overline{w}'(y,z)}{|x-y|}dy \\ (6.9) \quad &\leq C(\|\nabla_1 w(\cdot,z)\| \cdot \|w(\cdot,z) - w'(\cdot,z)\| + \|\nabla_1 w'(\cdot,z)\| \cdot \|w(\cdot,z) - w'(\cdot,z)\|). \end{aligned}$$

Now the Cauchy-Schwarz inequality implies

$$\sup_{x\in\mathbb{R}^3} \int |I(x,z)|dz \leq C(\|w\|_{\mathbf{H}^1} + \|w'\|_{\mathbf{H}^1})\|w - w'\|_{\mathbf{H}^0}. \tag{6.10}$$

Hence, the second term on the right hand side of (6.8) also admits the bound (6.6). □

Next lemma extends these estimates to $\mathbf{H}^2$ norms.

LEMMA 6.3. (cf. Lemma 5 (b) of [**11**]) *For $w, w' \in H^2$*

$$\|F(w)\|_{\mathbf{H}^2} \leq C_F\|w\|^2_{\mathbf{H}^1}\|w\|_{\mathbf{H}^2}, \tag{6.11}$$

$$\|F(w) - F(w')\|_{\mathbf{H}^2} \leq C_F(\|w\|^2_{\mathbf{H}^2} + \|w'\|^2_{\mathbf{H}^2})\|w - w'\|_{\mathbf{H}^2}. \tag{6.12}$$

PROOF. i) To prove (6.11) we should bound the norms $\|F_1(w)\|_{\mathbf{H}^0}$, $\|\Delta F_1(w)\|_{\mathbf{H}^0}$, and $\|F_1(w)\Delta\|_{\mathbf{H}^0}$. The first and second norms are bounded similarly to Lemma 6.2. It remains to bound the third norm. Let us consider the integrand of (6.7):

$$F_z = w\int \frac{w(y,z)\overline{w}(y,z)}{|x-y|}dy. \tag{6.13}$$

This is the integral operator with the kernel

$$F_z(x,y') = w(x,y')\int \frac{w(y,z)\overline{w}(y,z)}{|y'-y|}dy \tag{6.14}$$

Further, $F_z\Delta$ is the integral operator with the kernel $\Delta_{y'}F_z(x,y') = \Delta_2 F_z(x,y')$. Now we differentiate (cf. Lemma 5 of [**11**]):

$$\begin{aligned} \Delta_2 F_z(x,y') &= 4\pi w(x,y')\cdot w(y',z)\overline{w}(y',z) + 2\nabla_2 w\int \frac{\nabla_1 w(y,z)\overline{w}(y,z)}{|x-y|}dy \\ &+2\nabla_2 w\int \frac{w(y,z)\nabla_1\overline{w}(y,z)}{|x-y|}dy + \Delta_2 w\int \frac{w(y,z)\overline{w}(y,z)}{|x-y|}dy. \end{aligned} \tag{6.15}$$

Here the first term on the right hand side is the operator with the integral kernel

$$K_z(x,y') = 4\pi w(x,y')w(y',z)\overline{w}(y',z). \tag{6.16}$$

Let us bound its Hilbert-Schmidt norm extending estimate (10) of [**11**] to the wave-matrix formalism: applying the Hölder inequality and the Sobolev embedding theorem, we obtain that

$$\begin{aligned} \int |K_z(x,y')|^2 dy' &\leq C\|w(x,\cdot)\|^2_{L^6}\|w(\cdot,z)\|^2_{L^6(\mathbb{R}^3)}\|\overline{w}(\cdot,z)\|^2_{L^6(\mathbb{R}^3)} \\ &\leq C\|w(x,\cdot)\|^2_{H^1(\mathbb{R}^3)}\|w(\cdot,z)\|^2_{H^1(\mathbb{R}^3)}\|\overline{w}(\cdot,z)\|^2_{H^1(\mathbb{R}^3)}. \end{aligned} \tag{6.17}$$

Integrating over $x \in \mathbb{R}^3$ we obtain

$$\|K_z\|_{\mathbf{H}^0} \le C\|w\|_{\mathbf{H}^1(\mathbb{R}^3)}\|w(\cdot,z)\|_{H^1(\mathbb{R}^3)}\|\overline{w}(\cdot,z)\|_{H^1(\mathbb{R}^3)}. \tag{6.18}$$

Finally, integrating over $z \in \mathbb{R}^3$ we obtain by the Cauchy-Schwarz the bound (6.11) for the contribution of the first term on the right hand side (6.15). The bounds for the other three terms can be obtained by the same Cauchy-Schwarz trick using the bounds of type (6.4) for the corresponding integrals.

ii) It suffices to prove (6.12) for F_1. Obviously,

$$\begin{aligned}\|F_1(w)-F_1(w')\|_{\mathbf{H}^2} \\ \sim \|F_1(w)-F_1(w')\|_{\mathbf{H}^0} + \|\Delta[F_1(w)-F_1(w')]\|_{\mathbf{H}^0} + \|[F_1(w)-F_1(w')]\Delta\|_{\mathbf{H}^0}.\end{aligned} \tag{6.19}$$

The first term on the right hand side is estimated by (6.6). For the second term the estimate follows from (6.8) by the same arguments (6.9)–(6.10). Finally, the estimate for the last term follows by the combination of the arguments (6.9)–(6.10) with the proof of (6.11) above. □

7. Integral Duhamel equation

Let us reduce (5.5) with $w(\cdot) \in X$ to an equivalent integral equation. Using notations (5.1), we rewrite (5.5) as

$$i\dot{w}(t) = \{H_0, w(t)\} + \{\tilde{V}(t), w(t)\}. \tag{7.1}$$

We reduce this equation to the case of bounded generator withdrawing its unbounded part. Namely, let us write the solution in the "interaction picture"

$$w(t) = U_0(t)C(t)U_0(t),\ t \in \mathbb{R}, \tag{7.2}$$

where $U_0(t) := \exp(-iH_0t)$ is the dynamical group of the "free" Schrödinger equation. Obviously, $C(\cdot) \in X$ since $w(\cdot) \in X$. Hence, the differentiation gives

$$\dot{w}(t) = \{H_0, w(t)\} + U_0(t)\dot{C}(t)U_0(t). \tag{7.3}$$

Substituting into (5.5), we obtain the equivalent reduced equation

$$iU_0(t)\dot{C}(t)U_0(t) = \{\tilde{V}(t), w(t)\}. \tag{7.4}$$

The integration gives

$$C(t) = C(0) - i\int_0^t U_0(-s)\{\tilde{V}(s), w(s)\}U_0(-s)ds. \tag{7.5}$$

Coming back to $w(t)$, we get the integral "Duhamel" equation

$$w(t) = U_0(t)w(0)U_0(t) - i\int_0^t U_0(t-s)\{\tilde{V}(s), w(s)\}U_0(t-s)ds,\ t \in \mathbb{R}. \tag{7.6}$$

LEMMA 7.1. *For $w(\cdot) \in X$ the differential equation (5.5) is equivalent to its integral version (7.6).*

PROOF. To deduce (7.4) from (7.5) for $w(\cdot) \in X$ it suffices to note that the integrand belongs to $C_s(\mathbb{R}, \mathbf{H}^2)$ (strongly continuous operator functions) since

$$\{\tilde{V}(t), w(t)\} \in C(\mathbb{R}, \mathbf{H}^2) \tag{7.7}$$

by (6.12). □

8. Local solutions

Let us prove that the local solution exists by the Picard fix point theorem due to the Lipschitz continuity. Let us denote $X_\varepsilon := C^1_s(-\varepsilon,\varepsilon;\mathbf{H}^0)\cap C(-\varepsilon,\varepsilon;\mathbf{H}^2)$ for $\varepsilon>0$.

LEMMA 8.1. *For any $w(0)\in\mathbf{H}^2$ there exists a unique strong solution $w(\cdot)\in X_\varepsilon$ to the equation (5.5) for $|t|<\varepsilon$ with $\varepsilon=\varepsilon(C_F,\|w(0)\|_{\mathbf{H}^2})>0$.*

PROOF. Operators $U_0(t)$ are uniformly bounded in $H^2(\mathbb{R}^3)$. Hence, due to (6.11) and (6.12) the unique solution $w(\cdot)\in C(-\varepsilon,\varepsilon;\mathbf{H}^2)$ to the integral equation (7.6) exists by the Picard fix point theorem for $|t|<\varepsilon$ with $\varepsilon=\varepsilon(C_F,\|w(0)\|_{\mathbf{H}^2})>0$ (see [**31**]). It remains to prove that

$$w(\cdot)\in C^1_s(-\varepsilon,\varepsilon;\mathbf{H}^0). \tag{8.1}$$

Indeed, let us consider both terms on the right hand side of (7.6). The first term belongs to $C^1_s(-\varepsilon,\varepsilon;\mathbf{H}^0)$ since

$$\|\dot U_0(t)w(0)U_0(t)\|_{\mathbf{H}^0}+\|U_0(t)w(0)\dot U_0(t)\|_{\mathbf{H}^0}$$

$$\sim\ \|U_0(t)\tilde H_0w(0)U_0(t)\|_{\mathbf{H}^0}+\|U_0(t)w(0)\tilde H_0U_0(t)\|_{\mathbf{H}^0}, \tag{8.2}$$

where $\tilde H_0w(0)\in\mathbf{H}^0$ and $w(0)\tilde H_0\in\mathbf{H}^0$. Finally, the integrand (7.6) belongs to $C^1_s(-\varepsilon,\varepsilon;\mathbf{H}^2)$ since

$$\{\tilde V(t),w(t)\}\in C(-\varepsilon,\varepsilon;\mathbf{H}^2) \tag{8.3}$$

by (6.12). Hence, $w(\cdot)\in X_\varepsilon$, and (7.6) implies (5.5) for $|t|<\varepsilon$. □

9. Conservation laws

To deduce Theorem 5.3 from Lemma 8.1, we need a priori estimates which follow from energy and norm conservation.

9.1. Energy conservation. Let us prove the energy conservation

$$\tilde{\mathcal{E}}^{HF}(w(t))=\text{const},\ \ t\in\mathbb{R}. \tag{9.1}$$

Formally, the conservation follows by direct differentiation from the Hamilton structure of the equation (4.7). However, the formal differentiation cannot be justified with the application of the standard chain rule due to a mismatch in the estimates for the remainder. This is why we justify the differentiation directly using the polynomial structure of the Hamilton functional.

LEMMA 9.1. *Let $w(\cdot)\in X$ be a strong solution to (5.5). Then the energy conservation (9.1) holds.*

PROOF. Let us write the reduced energy (5.2) for the solution $w(t)$ as

$$\tilde{\mathcal{E}}^{RHF}(w(t))=\frac14\operatorname{tr}[H_0w(t)w^*(t)+H_0w^*(t)w(t)]+\frac14\int\frac{\tilde\rho(x,t)\tilde\rho(y,t)}{|x-y|}dxdy. \tag{9.2}$$

Here the operators H_0, $w(t)$ and $w^*(t)$ can be cyclically permuted. Hence, the derivative can be written formally as

$$\begin{aligned}\dot{\tilde{\mathcal{E}}}^{RHF}(w(t)) &= \frac{1}{4}\operatorname{tr}[w^*(t)H_0\dot w(t)+H_0w(t)\dot w^*(t)+w(t)H_0\dot w^*(t)\\ &\quad +H_0w^*(t)\dot w(t)]+\frac{1}{2}\langle\tilde V_e(x,t),\dot{\tilde\rho}(x,t)\rangle\\ &= \frac{1}{4}\operatorname{tr}[\{H_0,w(t)\}\dot w^*(t)+\{H_0,w^*(t)\}\dot w(t)]+\frac{1}{2}\langle\tilde V_e(x,t),\dot{\tilde\rho}(x,t)\rangle. \qquad (9.3)\end{aligned}$$

To justify this differentiation, we first show that all these terms exist. The terms with H_0 exist because $\dot w(t)\in\mathbf{H}^0$, and also $\{H_0,w(t)\}\in\mathbf{H}^0$ since $w(t)\in\mathbf{H}^2$. The last term can be written similarly,

$$\begin{aligned}\frac{1}{2}\langle\tilde V_e(x,t),\dot{\tilde\rho}(x,t)\rangle &= \frac{1}{4}\operatorname{tr}[\tilde V(t)(\dot w(t)w^*(t)+w(t)\dot w^*(t)+\dot w^*(t)w(t)+w^*(t)\dot w(t))]\\ &= \frac{1}{4}\operatorname{tr}[\{\tilde V(t),w(t)\}\dot w^*(t)+\{\tilde V(t),w^*(t)\}\dot w(t)]. \qquad (9.4)\end{aligned}$$

This expression is finite since $\tilde V(t)$ is the operator of multiplication by $e\tilde V_e(\cdot,t)$ which is the bounded function by (6.2).

Now we can justify the differentiations (9.3). Since the energy is the fourth order polynomial in $w(t)$ and $w^*(t)$, the increment $\Delta\tilde{\mathcal{E}}^{RHF}(t):=\tilde{\mathcal{E}}^{RHF}(w(t+\Delta t))-\tilde{\mathcal{E}}^{RHF}(w(t))$ can be written as the corresponding polynomial in $w(t),w^*(t)$, and $\Delta w(t):=w(t+\Delta t)-w(t)$. The main part, linear in $\Delta w(t)$, looks like (9.3)-(9.4) with $\dot w(t)$ substituted by $\Delta w(t)$ and $\dot w^*(t)$ substituted by $\Delta w^*(t)$. It remains to divide $\Delta\tilde{\mathcal{E}}^{RHF}(t)$ by Δt and send $\Delta t\to 0$. Then the contribution of the main part gives (9.3)-(9.4) by previous arguments. The contributions of the higher order terms converge to zero by similar arguments.

Finally, let us prove that the derivative (9.3) vanishes using the dynamic equation (5.5). First let us rewrite (9.3)-(9.4) as

$$\dot{\tilde{\mathcal{E}}}^{RHF}(w(t))=\frac{1}{4}\operatorname{tr}[\{H_0+\tilde V(t),w^*(t)\}\dot w(t)+\{H_0+\tilde V(t),w(t)\}\dot w^*(t)]. \qquad (9.5)$$

Substituting here $\dot w(t)=-i\{H_0+\tilde V(t),w(t)\}$ and $\dot w^*(t)=i\{H_0+\tilde V(t),w^*(t)\}$, we obtain zero since $w(t)\in\mathbf{H}^2$, and hence both anticommutators $\{H_0+\tilde V(t),w(t)\}$ and $\{H_0+\tilde V(t),w^*(t)\}$ are the Hilbert-Schmidt operators. □

9.2. Charge conservation. Now we can prove the charge conservation:

$$Q(t):=\int\tilde\rho(x,t)dx=\text{const},\ t\in\mathbb{R}. \qquad (9.6)$$

LEMMA 9.2. *Let $w(\cdot)\in X$ be a strong solution to (5.5). Then the charge conservation (9.6) holds.*

PROOF. First, we note that $Q(t)=e\operatorname{tr}\tilde K(t)=e\operatorname{tr}w(t)w^*(t)=e\operatorname{tr}C(t)C^*(t)$ by (7.2) since the operators $U_0(t)$ are unitary. So it remains to prove the conservation of $\operatorname{tr}C(t)C^*(t)$ which follows by the differentiation. Namely, (7.4) implies

$$i\dot C(t)=V_L(t)C(t)+C(t)V_R(t),\ V_L(t)=U_0^*(t)\tilde V(t)U_0(t),\ V_R(t)=U_0(t)\tilde V(t)U_0^*(t). \qquad (9.7)$$

Here the selfadjoint operators $V_L(t), V_R(t) \in C_s(\mathbb{R}, \mathcal{L})$ by the bounds of type (6.2) for differences $\tilde{V}_e(x, t+\Delta t) - \tilde{V}_e(x,t)$, where $\mathcal{L} = \mathcal{L}(L^2, L^2)$ is the space of bounded operators in L^2, and $C_s(\mathbb{R}, \mathcal{L})$ denotes the space of strongly continuous operator functions. Taking the adjoint to both sides, we obtain $-i\dot{C}^*(t) = C^*(t)V_L(t) + V_R(t)C^*(t)$, and hence

$$i\frac{d}{dt}[C(t)C^*(t)] = [V_L(t), C(t)C^*(t)]. \tag{9.8}$$

Therefore, $\operatorname{tr} C(t)C^*(t) = \text{const}$ since the trace of the commutator vanishes. □

9.3. Norm conservation. Let us note that (9.6) means that $\|w(t)\|_{\mathbf{H}^0} = \text{const}$. Further we will prove also the conservation of the operator norm in $\mathcal{L}$:

$$\|w(t)\| = \text{const}, \ t \in \mathbb{R}. \tag{9.9}$$

Proposition 9.3. Let $w(\cdot) \in X$ be a strong solution to (5.5). Then the norm conservation (9.9) holds.

Proof. For the proof we need the following lemma.

Lemma 9.4. *Let $w(\cdot) \in X$ be a strong solution to (5.5), and $V_L(t)$, $V_L(t \in C(\mathbb{R}, \mathcal{L})$ are the corresponding selfadjoint operators (9.7). Then*

i) There exist unique unitary propagators $U_L(t,s)$ and $U_R(t,s)$ which are solutions to

$$i\dot{U}_L(t,s) = V_L(t)U_L(t,s), \ t,s \in \mathbb{R}; \ U_L(s,s) = I \tag{9.10}$$

$$i\dot{U}_R(t,s) = U_R(t,s)V_R(t), \ t,s \in \mathbb{R}; \ U_R(s,s) = I, \tag{9.11}$$

where the derivatives are understood in the strong sense.

ii) The "group identities" hold

$$U_L(t,s)U_L(s,r) = U_L(t,r), \ U_R(t,s)U_R(s,r) = U_R(t,r), \ t,s,r \in \mathbb{R}. \tag{9.12}$$

Proof. The solutions exist and are unique since $V_L(t), V_R(t) \in C(\mathbb{R}, \mathcal{L})$. The identity (9.12) holds by the uniqueness of the solutions.

The propagators are unitary operators since the generators $V_L(t)$, $V_R(t)$ are self-adjoint. For example, the adjoint equation to (9.10) reads $\dot{U}_L^*(t,s) = iU_L^*(t,s)V_L(t)$, and hence

$$\begin{aligned} \frac{d}{dt}[U_L^*(t,s)U_L(t,s)] &= \dot{U}_L^*(t,s)U_L(t,s) + U_L^*(t,s)\dot{U}_L(t,s) \\ &= iU_L^*(t,s)V_L(t,s)U_L(t,s) - iU_L^*(t,s)V_L(t)U_L(t,s) = 0. \end{aligned} \tag{9.13}$$

Therefore, $U_L^*(t,s)U_L(t,s) = U_L^*(s,s)U_L(s,s) = I$. Finally, the operator $U_L(t,s)$ is invertible by (9.12) with $r = t$. □

Corollary 9.5. Any strong solution $C(\cdot) \in X$ to (9.7) admits the representation $C(t) = U_L(t)C(0)U_R(t)$ by the uniqueness of the solution. Respectively, any strong solution $w(\cdot) \in X$ to (5.5) admits the representation

$$w(t) = U_0(t)U_L(t)U_0^*(t)w(0)U_0^*(t)U_R(t)U_0(t), \ t \in \mathbb{R}. \tag{9.14}$$

Now the norm conservations (9.9) obviously hold since all the operators $U_0(t)$, $U_L(t)$ and $U_R(t)$ are unitary. □

10. A priori estimates and global solutions

The conservation laws imply the following a priori estimates.

LEMMA 10.1. *Let $w(\cdot) \in X_\varepsilon$ be a strong solution to equation (5.5) for $|t| < \varepsilon$ with an $\varepsilon > 0$. Then*

$$\|w(t)\|_{\mathbf{H}^1} \leq C_1, \ t \in (-\varepsilon, \varepsilon). \tag{10.1}$$

$$\|w(t)\|_{\mathbf{H}^2} \leq C_2 e^{C_3|t|}, \ t \in (-\varepsilon, \varepsilon). \tag{10.2}$$

where the constants C_1, C_2, and C_3 depend only on $\|w(0)\|_{\mathbf{H}^2}$.

PROOF. We follow the scheme of [**11**, Section 3.4]:

i) The first estimate follows from the energy conservation (9.2) since the last term is nonnegative while the operator H_0 generates the Sobolev norm H^1.

ii) The second estimate follows from the integral equation (7.6). Namely,

$$\|w(t)\|_{\mathbf{H}^2} \leq C[\|w(0)\|_{\mathbf{H}^2} + \int_0^t \|\{\tilde{V}(s), w(s)\}\|_{\mathbf{H}^2} ds], \ t \in (-\varepsilon, \varepsilon). \tag{10.3}$$

Now using (6.11), we obtain

$$\|w(t)\|_{\mathbf{H}^2} \leq C[\|w(0)\|_{\mathbf{H}^2} + C_F \int_0^t \|w(s)\|^2_{\mathbf{H}^1} \|w(s)\|_{\mathbf{H}^2}] ds, \ t \in (-\varepsilon, \varepsilon). \tag{10.4}$$

Hence, (10.2) follows by the Gronwall lemma and (10.1). □

Proof of Theorem 5.3. Lemmas 8.1 and 10.1 imply Theorem 5.3 by standard arguments.

11. Agreement with the density matrix formalism

Let us discuss the agreement of the wave-matrix picture with the density matrix formalism. First of all, the basic quantities (4.6) coincide when $w(t)$ is Slater-type density matrix $w(t) = \sum_1^N |\psi_k(t)\rangle\langle\psi_k(t)|$ with the constraints (2.4). In this case also $\tilde{H}(t) = H(t)$.

Moreover, the density matrix (4.1) is invariant with respect to the transformation $w \mapsto Uw$ with any unitary operator U in X.

Further let us consider separately the static and dynamic aspects.

Static aspects. Next lemma means the complete agreement between the wave-matrix and the density-matrix formalism in the ground state problem.

LEMMA 11.1. *The ground state energy (2.18) in the density-matrix theory and the wave-matrix picture coincide:*

$$E^{HF} = \min\{\tilde{\mathcal{E}}^{HF}(w) : \|w\| \leq 1, \ \operatorname{tr} ww^* = N\}. \tag{11.1}$$

PROOF. i) (11.1) follows from (2.18) since $\tilde{\mathcal{E}}^{HF}(w) = \mathcal{E}^{HF}(\tilde{K})$ by (4.5) and (2.8), where $\tilde{K} := \frac{1}{2}[ww^* + w^*w] \geq 0$, and $\operatorname{tr} \tilde{K} := \operatorname{tr} ww^* = \operatorname{tr} w^*w = N$. □

Dynamical aspects.

LEMMA 11.2. *Let $w(\cdot) \in X$ be a strong solution to (5.5) with $\operatorname{tr} w(0)w^*(0) = N$ and $\|w(0)\| \leq 1$. Then the properties (2.7) hold for the density matrices $\tilde{K}(t) := \frac{1}{2}[w(t)w^*(t) + w^*(t)w(t)]$ and $K(t) := w(t)w^*(t)$ for all $t \in \mathbb{R}$.*

PROOF. Obviously,

$$\tilde{K}(t) \geq 0,\ K(t) \geq 0. \tag{11.2}$$

Further, $\operatorname{tr} \tilde{K}(t) = \operatorname{tr} K(t)$, and we know from Lemma 9.2 and its proof that

$$\operatorname{tr} \tilde{K}(t) = \operatorname{tr} K(t) = N \tag{11.3}$$

if $\operatorname{tr} K(0) = N$. It remains to note that

$$\|\tilde{K}(t)\| \leq 1,\ \|K(t)\| \leq 1,\ t \in \mathbb{R} \tag{11.4}$$

since $\|w(t)\| \leq 1$ by (9.9). □

Let us recall in conclusion that the dynamics (4.10) for the wave matrix $w(t)$ agrees with the von Neumann equation (3.4) for the corresponding density matrix $K(t) := w(t)w^*(t)$, see Remark 5.4.

Appendix A. Energy variation in wave-matrix picture

We prove Lemma 5.2. The Gâteaux differentiability of the energy $\tilde{\mathcal{E}}^{RHF}(w)$ for $w \in \mathbf{H}^2$ follows by the same arguments which justify the differentiation in time (9.3). Hence, to justify (5.6), it suffices to differentiate formally each term on the right hand side of (5.2). Additionally, we will differentiate also the "exchange term" of (4.5).

I. For the first term $I_1 = -\frac{1}{4}[\langle \Delta_x w(x,y), w(x,y)\rangle + \langle \Delta_y w(x,y), w(x,y)\rangle$ the variation is obvious:

$$D_{\overline{w}(x,y)} I_1 = -\frac{1}{2}[\Delta_x w(x,y) + \Delta_y w(x,y)], \tag{A.1}$$

which is the integral kernel of the anticommutator $\frac{1}{2}\{-\Delta, w\}$.

II. For the second term $I_2 = \dfrac{e}{4}\displaystyle\int\int [V_n(x) + V_n(y)]|w(x,y)|^2 dxdy$ the variation is also obvious:

$$D_{\overline{w}(x,y)} I_2 = \frac{e}{2}[V_n(x) + V_n(y)]w(x,y), \tag{A.2}$$

which is the integral kernel of the anticommutator $\frac{1}{2}\{eV_n, w\}$.

III. For the third term $I_3 = \dfrac{1}{4}\displaystyle\int\int \frac{\tilde{\rho}(x')\tilde{\rho}(y')}{|x'-y'|} dx'dy'$ the variation reads

$$D_{\overline{w}(x,y)} I_2 = \frac{1}{2}\int\int \frac{\tilde{\rho}(y')}{|x'-y'|} D_{\overline{w}(x,y)}\tilde{\rho}(x')dx'dy'. \tag{A.3}$$

Definition (4.3) implies that

$$\begin{aligned} D_{\overline{w}(x,y)}[\tilde{\rho}(x')] &= \frac{e}{2} D_{\overline{w}(x,y)} \int [w(x',z)\overline{w(x',z)} + \overline{w(z,x')}w(z,x')]dz \\ &= e[\delta(x'-x)w(x',y) + \delta(x'-y)w(x,x')] \end{aligned} \tag{A.4}$$

Substitution into (A.3) gives

$$D_{\overline{w}(x,y)}I_2 = \frac{e}{2}\int\int \frac{\tilde\rho(y')}{|x'-y'|}[\delta(x'-x)w(x',y)+\delta(x'-y)w(x,x')]dx'dy'$$

$$= \frac{e}{2}\int \frac{\tilde\rho(y')}{|x-y'|}w(x,y)dy' + \frac{e}{2}\int \frac{\tilde\rho(y')}{|y-y'|}w(x,y)dx', \tag{A.5}$$

which is the integral kernel of the anticommutator $\frac{e}{2}\{\tilde V, w\}$, where the potential $\tilde V(x)$ is defined according to (4.9):

$$\tilde V(x) = \int \frac{\tilde\rho(y)}{|x-y|}dy. \tag{A.6}$$

IV. Similarly, for the exchange term, $I_4 = -\frac{1}{4}\int\int \frac{|\tilde\tau(x',y')|^2}{|x'-y'|}dx'dy'$, the variation reads

$$D_{\overline{w}(x,y)}I_4 = -\frac{1}{4}\int\int \frac{\tilde\tau(x',y')D_{\overline{w}(x,y)}\tilde\tau(y',x') + \tilde\tau(y',x')D_{\overline{w}(x,y)}\tilde\tau(x',y')}{|x'-y'|}dx'dy' \tag{A.7}$$

by (4.3). Definition (4.3) implies that

$$D_{\overline{w}(x,y)}\tilde\tau(x',y') = \frac{e}{2}D_{\overline{w}(x,y)}\int [w(x',z)\overline{w(y',z)} + \overline{w(z,x')}w(z,y')]dz$$

$$= e[\delta(y'-x)w(x',y)+\delta(x'-y)w(x,y')]. \tag{A.8}$$

Substitution into (A.7) gives

$$D_{\overline{w}(x,y)}I_4 = -\frac{e}{4}\int\int \frac{\tilde\tau(x',y')[\delta(x'-x)w(y',y)+\delta(y'-y)w(x,x')]}{|x'-y'|}dx'dy'$$

$$-\frac{e}{4}\int\int \frac{\tilde\tau(y',x')[\delta(y'-x)w(x',y)+\delta(x'-y)w(x,y')]}{|x'-y'|}dx'dy'$$

$$= -\frac{e}{4}\int\int \frac{\tilde\tau(x,y')w(y',y)}{|x-y'|}dy' - \frac{e}{4}\int\int \frac{\tilde\tau(x',y)w(x,x')}{|x'-y|}dx'$$

$$-\frac{e}{4}\int\int \frac{\tilde\tau(x,x')w(x',y)}{|x'-x|}dx' - \frac{e}{2}\int\int \frac{\tilde\tau(y',y)w(x,y')}{|y-y'|}dy'$$

$$= -\frac{e}{2}\int\int \frac{\tilde\tau(x,y')w(y',y)}{|x-y'|}dy' - \frac{e}{2}\int\int \frac{\tilde\tau(x',y)w(x,x')}{|x'-y|}dx', \tag{A.9}$$

which is the integral kernel of the anticommutator $\frac{e}{2}\{\tilde{\mathcal{T}}, w\}$ where the operator $\tilde{\mathcal{T}}$ is defined according to (4.9).

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