ASC Report No. 04/2008

Analysis and Time Integration of the Multi-Configuration Time-Dependent Hartree-Fock Equations in Electronic Dynamics

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www.asc.tuwien.ac.at ISBN 978-3-902627-00-1

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ISBN 978-3-902627-00-1

ANALYSIS AND TIME INTEGRATION OF THE MULTI-CONFIGURATION TIME-DEPENDENT HARTREE-FOCK EQUATIONS IN ELECTRON DYNAMICS

OTHMAR KOCH AND CHRISTIAN LUBICH

ABSTRACT. We discuss existence, regularity and numerical approximation of the solution to the multi-configuration time-dependent Hartree-Fock (MCT-DHF) equations in quantum dynamics. This method approximates the high-dimensional solution to the time-dependent electronic Schrödinger equation by a linear combination of products of functions depending only on a single degree of freedom. The equations of motion, obtained via the Dirac–Frenkel time-dependent variational principle, consist of a coupled system of low-dimensional nonlinear partial differential equations and ordinary differential equations. We show that the MCTDHF equations have a global solution in the Sobolev space H^2 if the initial data has the same regularity. Moreover, we investigate the convergence of a time integrator based on splitting of the vector field. First order convergence in the H^1 norm and second order convergence in L^2 are established.

CONTENTS

Date: February 12, 2008.

1991 *Mathematics Subject Classification.* 35F25, 58J90, 65M12, 81V55.

Key words and phrases. MCTDHF method, electronic Schrödinger equation, regularity, splitting methods.

Supported by the Austrian Academy of Sciences, APART program.

Introduction

This paper deals with an approach to the approximate solution of the time-dependent Schrödinger equation for a system of unbound fermions interacting by Coulomb forces,

$$\mathrm{i}\,\frac{\partial\psi}{\partial t} = H\psi, \qquad \psi(0) = \psi_0, \tag{1}$$

where the wave function $\psi = \psi(x^{(1)}, \dots, x^{(f)}, t)$ depends on the spatial coordinates $x^{(k)} \in \mathbb{R}^3$ of f particles, and on time t. In atomic units, the Hamiltonian is given by

$$H := \sum_{k=1}^{f} \left(-\frac{1}{2}\Delta^{(k)} + \sum_{l<k} V(x^{(k)} - x^{(l)}) \right) = \sum_{k=1}^{f} T^{(k)} + V = T + V, \tag{2}$$

where

$$V(x-y) := \frac{1}{|x-y|} = \frac{1}{\sqrt{(x_1-y_1)^2 + (x_2-y_2)^2 + (x_3-y_3)^2}}, \tag{3}$$

and $\Delta^{(k)}$ is the Laplace operator w. r. t. $x^{(k)}$ only (we will omit the superscripts of T and Δ where the operand is clear). The particle-particle interactions are described by the singular *Coulomb potential* V.

The applications that motivate this research are given by the study of ultrafast laser pulses in photonics [8, 20, 40, 41], where the kinetic part of the Hamiltonian additionally depends on a time-dependent drift term modeling the laser, and moreover a nuclear attractive potential is incorporated,

$$T^{(k)} := \frac{1}{2}\left(-\mathrm{i}\nabla^{(k)} - A(t) \right)^2 + U(x^{(k)}), \tag{4}$$

with

$$U(x) := -\frac{Z}{|x|} = -\frac{Z}{\sqrt{x_1^2 + x_2^2 + x_3^2}}, \quad Z \in \mathbb{N}.$$

The modifications necessary for the treatment of these extended models are briefly discussed in the appendix.

Our method of choice to make the original, linear electronic Schrödinger equation (1) tractable for numerical computation, is the multiconfiguration time-dependent Hartree–Fock method, MCTDHF [8, 19, 20, 33, 40, 41], which is closely related to the MCTDH method in quantum molecular dynamics [3, 4, 7, 30, 31, 39].

In the MCTDHF approach, the wave function is approximated by an antisymmetric linear combination of products of functions (also denoted as *Slater determinants*) each depending on the coordinates of only a single particle, or of a single degree of freedom (henceforth often referred to as *orbitals*). The antisymmetry is a consequence of the *Pauli exclusion principle* [26]. The Dirac–Frenkel time-dependent variational principle [11, 12] yields equations of motion for the single-particle functions and the coefficients in the linear combination of the products. The MCTDHF method thus replaces the high-dimensional linear Schrödinger equation by a system of low-dimensional nonlinear partial differential equations and ordinary differential equations and in this way makes the problem computationally tractable.

In Section 3 of this report, we study the nonlinear equations of motion of the MCTDHF approach. For initial data in the Sobolev space H^2 of functions that are square

integrable together with all their first and second-order weak partial derivatives, we show that a unique solution to the MCTDHF equations exists globally in H^2.
In Section 4, we study the approximation of the MCTDHF equations by time semi-discretization employing an operator splitting introduced in [28]. It is shown that for a symmetric, second-order splitting, first order convergence holds in H^1 when the exact solution is in H^2, and the method is second order convergent in L^2 if the exact solution is in H^3.

1. The MCTDHF method

In the MCTDHF method, the multi-particle wave function ψ is approximated by an antisymmetric linear combination of Hartree products, that is, for $x = (x^{(1)}, \dots, x^{(f)})$,

$$\begin{aligned} \psi(x,t) \quad &\approx \quad u(x,t) = \sum_J a_J(t)\, \Phi_J(x,t) \\ &= \sum_{(j_1,\dots,j_f)} a_{j_1,\dots,j_f}(t)\, \phi_{j_1}(x^{(1)},t) \cdots \phi_{j_f}(x^{(f)},t). \end{aligned} \tag{5}$$

Here, the multi-indices $J = (j_1, \dots, j_f)$ formally vary for $j_k = 1, \dots, N$, $k = 1, \dots, f$, the $a_J(t)$ are complex coefficients depending only on t, and the *single-particle functions* $\phi_{j_k}(x^{(k)}, t)$ (also referred to as *orbitals*) depend on the coordinates $x^{(k)}$ of a single particle and on time t. However, the Pauli principle implies antisymmetry in the coefficients a_J. Thus, in fact only $\binom{N}{f}$ coefficients a_J have to be determined in the actual computations. The MCTDHF method is a model reduction analogous to the low rank approximation of matrices, where a large system matrix is replaced by a linear combination of rank-1 matrices $v \otimes w$ [24].
The Dirac–Frenkel variational principle [11, 12] is used to derive differential equations for the coefficients a_J and the single-particle functions ϕ_j in (5). Thus, for u in the manifold $\mathcal{M}$ of ansatz functions (5), we require

$$\left\langle \delta u \,\middle|\, \mathrm{i}\frac{\partial u}{\partial t} - Hu \right\rangle = 0, \tag{6}$$

where δu varies in the tangent space $\mathcal{T}_u\mathcal{M}$ of $\mathcal{M}$ at u.
This variational approximation procedure is discussed in its abstract form in [25]. In the present paper, we are going to give an analysis of the MCTDHF equations of motion derived in the following, and discuss their numerical approximation by splitting methods.
Using the Dirac–Frenkel principle [11, 12] and imposing additional orthogonality constraints on the single-particle functions $\phi_j(x,t)$,

$$\langle \phi_j | \phi_k \rangle = \delta_{j,k}, \quad t \geq 0, \tag{7}$$

$$\left\langle \phi_j \,\middle|\, \frac{\partial \phi_l}{\partial t} \right\rangle = -\mathrm{i}\, \langle \phi_j \,|\, T \,|\, \phi_l \rangle, \quad t \geq 0, \tag{8}$$

yields a system of coupled ordinary and partial differential equations for the coefficients $a = (a_J)_J$ and single-particle functions $\phi = (\phi_j)_j$, rigorously derived in

[3, 30] under the implicit assumption that a sufficiently regular solution exists:

$$\mathrm{i}\,\frac{da_J}{dt} = \sum_K \langle \Phi_J | V | \Phi_K \rangle\, a_K =: \mathcal{A}_V(\phi)a, \quad \forall J, \tag{9}$$

$$\begin{aligned} \mathrm{i}\,\frac{\partial \phi_j}{\partial t} &= T\phi_j + (1-P)\sum_{l=1}^{N}\sum_{m=1}^{N} \rho_{j,m}^{-1} \langle \psi_m | V | \psi_l \rangle \phi_l \\ &=: T\phi + \mathcal{B}_V(a,\phi), \quad j = 1,\dots,N, \end{aligned} \tag{10}$$

where we define $\Phi_J := \prod_{k=1}^{f} \phi_{j_k}(x^{(k)})$, and the *single-hole functions*

$$\psi_j := \langle \phi_j \,|\, u \rangle, \quad j = 1,\dots,N. \tag{11}$$

The inner products $\langle \psi_m | V | \psi_l \rangle$ are over all variables except one, and P is the orthogonal projector onto the space spanned by $\phi_1,\dots,\phi_N$,

$$P = \sum_{j=1}^{N} |\phi_j\rangle\langle\phi_j|.$$

Finally,

$$\rho_{j,l} := \langle \psi_j | \psi_l \rangle \tag{12}$$

denotes the *density matrix* which is assumed to be nonsingular[1]. This problem formulation based on (8) offers the advantage that in the second equation the single particle operators $T^{(k)} \equiv T = -\frac{1}{2}\Delta + U$ appear outside the projection. For the system (9) and (10), we will prove the following result in Section 3:

Theorem 1.1. *Consider the system* (9)–(10) *together with initial conditions* $u(0) = u_0 \in \mathcal{M}$ *chosen such that the orthonormality constraints* (7) *are satisfied and the density matrix* ρ *defined in* (12) *is nonsingular. If the initial data for* ϕ_j *is in the Sobolev space* H^2*, then there exists a unique classical solution of the MCTDHF equations* (9)–(10) *satisfying*

$$a_J \in C^2([0,t^*),\mathbb{C}), \qquad \phi_j \in C^1([0,t^*),L^2) \cap C([0,t^*),H^2),$$

where either $t^* = \infty$ *or* ρ *becomes singular for* $t = t^*$*. Moreover, for* u *defined by* a_J*,* ϕ_j *via* (5)*, we have* $u(t) \in H^2$ *for* $t \in [0,t^*)$*, and* u *solves the Dirac–Frenkel variational equation* (6)*.*

Moreover, we will analyze the convergence of a time integrator based on splitting of the vector field [28]. The convergence result can be formulated in the following theorem:

Theorem 1.2. *Consider the numerical approximation of* (9)–(10) *given by time semidiscretization with the variational splitting method from* Section 4.1*,* $u_j \mapsto u_{j+1} = \mathcal{S}_{\Delta t} u_j$*,* $j = 0,1,\dots$*. Then the convergence estimates*

$$\|u_n - u(t_n)\|_{H^1} \le \text{const.}\Delta t, \qquad \text{for } t_n = n\Delta t, \tag{13}$$

$$\|u_n - u(t_n)\|_{L^2} \le \text{const.}(\Delta t)^2, \tag{14}$$

hold if the exact solution satisfies $u \in H^2$ *for* (13) *and* $u \in H^3$ *for* (14)*.*

[1] The choice of the initial condition such that ρ is nonsingular ensures that this holds at least for small t. In [2] a criterion for global invertibility of ρ is given.

2. Preliminaries

We start by repeating some elementary notions from functional analysis, see for example [6, 13, 32].
The underlying space we consider is $L^2 = L^2(\mathbb{R}^3)$ equipped with the inner product $\langle\cdot|\cdot\rangle$ and norm $\|\cdot\|$.

Definition 2.1. *$u \in L^2$ has a* weak derivative $\partial u \in L^2$ *if*

$$\langle w|\partial u\rangle = -\langle \partial w|u\rangle$$

for all test functions w.

Definition 2.2. *The set of all functions in L^2 having weak derivatives up to order $\leq k$ is denoted as the* Sobolev space H^k. *It is equipped with the norm*

$$\|u\|_{H^k} := \left(\sum_\alpha \|\partial^\alpha u\|^2\right)^{1/2},$$

where the sum is over all derivatives up to order k.

Furthermore, we will denote by $\|\cdot\|_{L^\infty}$ the supremum norm on the space of functions bounded almost everywhere.
If functions of several variables are considered, we will sometimes make clear what variables and spaces the inner products and norms refer to by writing

$$\langle\cdot|\cdot\rangle_{L^2(x)}, \quad \|\cdot\|_{H^k(x)}, \quad \ldots$$

In our analysis in Section 3 we will make strong use of the following results, see for instance [6]. Our formulations are specific to $\mathbb{R}^3$:

Theorem 2.1. *Let $k, m \in \mathbb{N}$ such that $k - m > 3/2$. Then for $u \in H^k$ there is a C^m function in the L^2 equivalence class of u and*

$$\|u\|_{C^m} := \sum \|\partial^\alpha u\|_{L^\infty} \leq \text{const.}\|u\|_{H^k},$$

where the sum is over all derivatives of order up to m.

This implies the following inequalities, see for instance [1], [6], [16], and [32]:

Corollary 2.1. *For $u, v \in H^2$, the following inequalities hold:*

$$\|uv\|_{L^2} \leq \|u\|_{L^2}\|v\|_{L^\infty} \leq \text{const.}\|u\|_{L^2}\|v\|_{H^2}, \tag{15}$$

$$\|uv\|_{H^1} \leq \text{const.}(\|u\|_{H^1}\|v\|_{H^2} + \|u\|_{H^2}\|v\|_{H^1}), \tag{16}$$

$$\|uv\|_{H^2} \leq \text{const.}\|u\|_{H^2}\|v\|_{H^2}, \tag{17}$$

$$\|uv\|_{L^2} \leq \text{const.}\|u\|_{L^4}\|v\|_{L^4} \leq \text{const.}\|u\|_{H^1}\|v\|_{H^1}. \tag{18}$$

$$\|uvw\|_{L^2} \leq \text{const.}\|u\|_{L^6}\|v\|_{L^6}\|w\|_{L^6} \leq \text{const.}\|u\|_{H^1}\|v\|_{H^1}\|w\|_{H^1}. \tag{19}$$

Moreover, we will use *Hardy's inequality* [18]

$$\int_{\mathbb{R}^3} \frac{|u(y)|^2}{|x-y|^2} dy \leq 4 \int_{\mathbb{R}^3} |\nabla u(y)|^2 dy, \quad x \in \mathbb{R}^3. \tag{20}$$

The following notions are discussed at length for instance in [18], [34].

Definition 2.3. *A one parameter family $S(t)$ of linear operators on a Banach space X is a* strongly continuous semigroup on X *if (i) $S(0) = I$ and (ii) $S(t+s) = S(t)S(s)$ and furthermore*

$$\lim_{t\to 0} S(t)x = x \qquad \forall x \in X.$$

Moreover, the linear operator A defined by

$$Ax := \lim_{t\to 0}(S(t)x - x)/t$$

with domain equal to the set of all x such that this limit exists, is denoted as the infinitesimal generator *of the semigroup $S(t)$.*

With this definition, it follows that the single-particle operator T from (2) generates a strongly continuous semigroup on H^2:

Theorem 2.2. *The single-particle operator T from* (2) *generates a strongly continuous semigroup $S(t) = \mathrm{e}^{-\mathrm{i}tT}$ on H^2 satisfying*

$$\|\mathrm{e}^{-\mathrm{i}tT}\phi\|_{L^2} \le \text{const.}\|\phi\|_{L^2} \quad \text{for } \phi \in L^2, \tag{21}$$

$$\|\mathrm{e}^{-\mathrm{i}tT}\phi\|_{H^1} \le \text{const.}\|\phi\|_{H^1} \quad \text{for } \phi \in H^1. \tag{22}$$

$$\|\mathrm{e}^{-\mathrm{i}tT}\phi\|_{H^2} \le \text{const.}\|\phi\|_{H^2} \quad \text{for } \phi \in H^2. \tag{23}$$

Remarks:

(1) The result can be concluded as follows: The operator Δ is defined on the domain H^2 [17], [18]. From [34] it follows that $S(t)x$ is in the domain of the infinitesimal generator A of S if x is, and $AS(t)x = S(t)Ax$.

(2) An analogous proposition also holds for the perturbed operator from (4), since ∇ is infinitesimally small with respect to Δ [35], and likewise for $1/|x|$ [18], and hence (4) also generates a semigroup on the same domain H^2, see also [17] and [22].

Definition 2.4. *A function $f : [0,T] \times X \to X$ is called* locally Lipschitz*, if for every $\hat{t} \ge 0$ and $c \ge 0$ there is a constant $L = L(c,\hat{t})$ such that*

$$\|f(t,u) - f(t,v)\| \le L\|u - v\| \tag{24}$$

holds for $u, v \in X$ with $\|u\|, \|v\| \le c$ and $t \le \hat{t}$.

Now, we consider the following abstract initial value problem on the Banach space X:

$$\dot{u}(t) + Au(t) = f(t, u(t)), \qquad u(0) = u_0 \in X. \tag{25}$$

The next theorem gives an existence result for this problem if f is *locally Lipschitz*:

Theorem 2.3. *Let $f : [0,\infty) \times X \to X$ be continuous in t for $t \ge 0$ and locally Lipschitz in u, uniformly in t on bounded intervals. If $-A$ is the infinitesimal generator of a strongly continuous semigroup $T(t)$ on X then for every u_0 in X there is a $t^* > 0$ such that the initial value problem* (25) *has a unique mild solution u on $[0, t^*)$. Moreover, if $t^* < \infty$, then*

$$\lim_{t\to t^*} \|u(t)\| = \infty.$$

Proof: See [34, p. 185]. □

In some of our following arguments, we are going to resort to the theory of *distributions* as a convenient tool, see for example [32, Section 3.3]. To this end, we first define the *delta function*:

Definition 2.5. *For $c \in \mathbb{R}^3$, the* delta function δ_c *is the distribution in $\mathbb{R}^3$ given by*

$$\delta_c(\phi) = \phi(c) \qquad \textit{for all test functions } \phi.$$

The delta function obeys the following rules [36]:

$$\langle \delta_x(y) | \phi(x) \rangle_{L^2(x)} = \langle \delta_y(x) | \phi(x) \rangle_{L^2(x)} = \phi(y), \tag{26}$$

$$\frac{d^p}{dy^p} \langle \delta_x(y) | \phi(x) \rangle_{L^2(x)} = (-1)^p \phi^{(p)}(y), \tag{27}$$

$$\Delta_y \frac{1}{|x-y|} = \delta_x(y). \tag{28}$$

3. Analysis of the MCTDHF equations

For our analysis of the MCTDHF equations (9)–(10), we assume that the components of $\phi(0)$ satisfy the orthonormality constraints (7). We will also assume that the components of $\phi(0) = \phi_0$ are in the Sobolev space H^2. Furthermore, our analysis is valid for all times such that the density matrix ρ in (12) is nonsingular. Note that our analysis proceeds similarly to that given in [9] and [10] in a different context. As the norms for the solution vectors we will use the following definitions: For coefficient vectors $a \in \mathbb{C}^n$, where $n := \binom{N}{f}$, we use the Euclidean norm

$$\|a\| = \Big(\sum_J |a_J|^2 \Big)^{1/2}. \tag{29}$$

For the single particle functions $\phi \in (L^2)^N$ we use

$$\|\phi\|_S = \max_j \|\phi_j\|_S, \tag{30}$$

where $\|\phi_j\|_S$ denotes the norm in either of the spaces $S = L^2,\ H^1,\ H^2$ etc. For the pair (a, ϕ), we use the norm

$$\|(a,\phi)\|_S = \max\{\|a\|, \|\phi\|_S\}. \tag{31}$$

In order to prove that the system (9)–(10) with initial data (a_0, ϕ_0) has a unique solution in H^2 at least for small t, we will show that this system satisfies the assumptions of Theorem 2.3. Subsequently, we will show that this solution remains bounded as long as ρ is nonsingular.

Proof of Theorem 1.1: First, we note that the right-hand side of (9)–(10) contains terms of the forms

$$\left\langle \phi_1(x) \left| \frac{1}{|x-y|} \right| \phi_2(x) \right\rangle_{L^2(x)} \tilde{\phi}_2(y) =: \mathcal{F}_1(y), \tag{32}$$

$$\left\langle \phi_1(x)\tilde{\phi}_1(y) \left| \frac{1}{|x-y|} \right| \phi_2(x)\tilde{\phi}_2(y) \right\rangle_{L^2(x,y)} =: \mathcal{F}_2, \tag{33}$$

which need to be estimated. These are associated with the particle-particle interactions V. Note that (33) appears only in the equations (9) since in (10) these contributions are annihilated by the projection $I - P$, and that the terms actually take the form of antisymmetric linear combinations

$$\left\langle \phi_1(x) \left| \frac{1}{|x-y|} \right| \phi_2(x)\tilde{\phi}_2(y) - \tilde{\phi}_2(x)\phi_2(y) \right\rangle_{L^2(x)} =: \mathfrak{S}_1(y), \tag{34}$$

$$\left\langle \phi_1(x)\tilde{\phi}_1(y) \left| \frac{1}{|x-y|} \right| \phi_2(x)\tilde{\phi}_2(y) - \tilde{\phi}_2(x)\phi_2(y) \right\rangle_{L^2(x,y)} =: \mathfrak{S}_2. \tag{35}$$

We start by estimating first the L^2-norm of (32), assuming that the single-particle functions appearing in its definition are in H^1.
First, we note that from the Cauchy-Schwarz inequality and (20) it follows

$$\left\| \left\langle \phi_1(x) \left| \frac{1}{|x-y|} \right| \phi_2(x) \right\rangle_{L^2(x)} \right\|_{L^\infty(y)} \leq \text{const.} \|\phi_1\|_{L^2} \|\phi_2\|_{H^1}. \tag{36}$$

Thus, by (15)

$$\|\mathcal{F}_1(y)\|_{L^2(y)} \quad \leq \quad \text{const.} \|\phi_1\|_{L^2} \|\phi_2\|_{H^1} \|\tilde{\phi}_2\|_{L^2}. \tag{37}$$

The modulus of (33) satisfies by similar arguments

$$\begin{aligned} |\mathcal{F}_2| \quad &\leq \quad \text{const.} \left| \left\langle \phi_1(x)\tilde{\phi}_1(y) \left| \frac{1}{|x-y|} \right| \phi_2(x)\tilde{\phi}_2(y) \right\rangle_{L^2(x,y)} \right| \\ &\leq \quad \text{const.} \left\| \left\langle \phi_1(x) \left| \frac{1}{|x-y|} \right| \phi_2(x) \right\rangle_{L^2(x)} \right\|_{L^\infty(y)} \left| \left\langle \tilde{\phi}_1 \middle| \tilde{\phi}_2 \right\rangle_{L^2} \right| \\ &\leq \quad \text{const.} \|\phi_1\|_{L^2} \|\phi_2\|_{H^1} \|\tilde{\phi}_1\|_{L^2} \|\tilde{\phi}_2\|_{L^2}. \end{aligned} \tag{38}$$

Thus, both (32) and (33) are bounded if the data are in H^1. Next, we consider the H^1-norm of the respective terms. For $\mathcal{F}_2$, there is nothing to do.
For (32), we proceed as follows: Noting that

$$\nabla_y \frac{1}{|x-y|} = \frac{1}{|x-y|^2} \overrightarrow{e}_{x-y},$$

where $\overrightarrow{e}_{x-y}$ denotes the unit vector in direction $x-y$, we find similarly as in (36)

$$\begin{aligned} \|\nabla_y \mathcal{F}_1(y)\|_{L^2} \quad &\leq \quad \text{const.} \left\| \left\langle \frac{1}{|x-y|}\phi_1(x) \middle| \overrightarrow{e}_{x-y} \middle| \frac{1}{|x-y|}\phi_2(x) \right\rangle_{L^2(x)} \right\|_{L^\infty(y)} \|\tilde{\phi}_2\|_{L^2} + \cdots \\ &\quad + \text{const.} \|\phi_1\|_{L^2} \|\phi_2\|_{H^1} \|\tilde{\phi}_2\|_{H^1} \\ &\leq \quad \left\| \left\| \frac{1}{|x-y|}\phi_1(x) \right\|_{L^2(x)} \right\|_{L^\infty(y)} \left\| \left\| \frac{1}{|x-y|}\phi_2(x) \right\|_{L^2(x)} \right\|_{L^\infty(y)} \|\tilde{\phi}_2\|_{L^2} + \cdots \\ &\quad + \text{const.} \|\phi_1\|_{L^2} \|\phi_2\|_{H^1} \|\tilde{\phi}_2\|_{H^1} \\ &\leq \quad \text{const.} \left(\|\phi_1\|_{H^1} \|\phi_2\|_{H^1} \|\tilde{\phi}_2\|_{L^2} + \|\phi_1\|_{L^2} \|\phi_2\|_{H^1} \|\tilde{\phi}_2\|_{H^1} \right). \end{aligned} \tag{39}$$

Again, the expression is bounded if all the data is in H^1 and thus $\mathcal{F}_1 \in H^1$.
Next, we use (26), (28) and (19) to obtain (this estimate is also given in [9, p.976])

$$\|\Delta_y \mathcal{F}_1(y)\|_{L^2} \quad \leq \quad \text{const.} \|\phi_1\|_{H^1} \|\phi_2\|_{H^1} \|\tilde{\phi}_2\|_{H^2}, \tag{40}$$

and $\mathcal{F}_1 \in H^2$ for H^2 data. Note in particular that the bound above depends only linearly on the H^2-norms of the ϕ's[2].
Finally, we need to verify that $\mathcal{F}_1$ is locally Lipschitz from $H^2 \to H^2$. To this end, the same estimates as above are used, where one of the ϕ's is replaced by the difference between two orbitals, respectively.
As the last step, we need to consider the dependence of $\mathcal{A}_V$ and $\mathcal{B}_V$ on the coefficient vector a. From the smooth dependence of ρ^{-1} on a when ρ is nonsingular, and the estimates for $\mathcal{F}_1$ and $\mathcal{F}_2$ above, it is clear that estimates

$$\|(\mathcal{A}_V(\phi)a, \mathcal{B}_V(a,\phi))^T - (\mathcal{A}_V(\tilde{\phi})\tilde{a}, \mathcal{B}_V(\tilde{a},\tilde{\phi}))^T\|_S \leq \mathcal{C}\|(a,\phi)-(\tilde{a},\tilde{\phi})\|_S, \tag{41}$$

hold locally in the spaces $S = L^2,\ H^1,\ H^2$, with a constant $\mathcal{C}$ depending on the H^1-norms of ϕ and $\tilde{\phi}$ and bounds on a and ρ^{-1}.
By this analysis, it is now clear that Theorem 2.3 can by applied to the system (9)–(10). Thus, we can conclude that a solution $\phi \in H^2$ exists on some interval $[0, t_1]$ with $t_1 > 0$. By the same arguments as in [25], this also implies that ϕ is a classical solution of (9)–(10). To see this, we note that the solution of (9)–(10) satisfies integral equations

$$a(t) = a(0) - \mathrm{i}\int_0^t \mathcal{A}_V(\phi(s))a(s)\,ds, \tag{42}$$

$$\phi(t) = \mathrm{e}^{-\mathrm{i}tT}\phi_0 - \mathrm{i}\int_0^t \mathrm{e}^{-\mathrm{i}(t-s)T}\mathcal{B}_V(a(s),\phi(s))\,ds. \tag{43}$$

Note that (43) results from a formal application of the variation of constant formula with the unitary evolution operator $\mathrm{e}^{-\mathrm{i}tT}$ of the free-particle Schrödinger equation. Next we apply T to (43) on noting that the expression $T\phi$ is well-defined since ϕ is in H^2. This yields that $t \mapsto (a(t),\phi(t))$ is continuously differentiable with time derivatives in L^2 and satisfies the system of differential equations (9)–(10).
This further implies that ϕ_j satisfy the orthonormality relations (7), provided that the initial data are orthonormal [25]. Hence, we conclude that $u = \sum_J a_J \Phi_J$ also solves the variational problem (6).
Having come this far, it can be concluded that the L^2 and the H^1 norms of u are bounded along solutions of (6). The L^2-norm is even conserved, which follows immediately noting the orthonormality constraints (8), see [23]. For the H^1 norm, first note that the energy $E := \langle u|H|u\rangle$ is conserved [25]. Moreover, the estimates

$$\|u\|^2_{H^1} \leq E \leq \text{const.}\|u\|^2_{H^1},$$

imply bounded H^1-norm.
To derive a bound for the H^2-norm, we apply T to (43), using the remark on page 6 and inserting the estimate (40), and we find that

$$\|\phi(t)\|_{H^2} \sim \|T\phi(t)\|_{L^2} \leq \|T\phi_0\|_{L^2} + \text{const.}(\|\phi\|_{L^2}, \|\phi\|_{H^1})\int_0^t \|\phi(\tau)\|_{H^2}\,d\tau. \tag{44}$$

Thus, from the *Gronwall lemma* [5] it follows that

$$\|\phi(t)\|_{H^2} \leq \|T\phi_0\|_{L^2}\exp(Ct), \tag{45}$$

[2] Taking into account the antisymmetry expressed in (34), the term

$$\left\langle \phi_1(x) \left| \Delta_y \frac{1}{|x-y|} \right| \phi_2(x)\tilde{\phi}_2(y) - \tilde{\phi}_2(x)\phi_2(y) \right\rangle_{L^2(x)}$$

vanishes, but this observation does not change our further arguments.

with a constant $C = C(\|\phi\|_{L^2}, \|\phi\|_{H^1})$ depending only on the L^2- and H^1-norms of ϕ. Since the latter have been shown to be bounded, we can conclude overall that ϕ can grow at worst exponentially in t, which in conjunction with Theorem 2.3 shows the assertion of Theorem 1.1.

4. Analysis of Variational Splitting

4.1. **Variational Splitting.** It has been suggested in [28] for a Hamiltonian $H = T + V$ as in (1) to use splitting methods to separate the computations in (9)–(10) for the single particle part T and the potential energy operator V.

One step of the variational splitting method starting at $u(t_0) = u_0$ with time step Δt is henceforth briefly denoted by $u_0 \mapsto u_1 = \mathcal{S}_{\Delta t} u_0$ and defined as follows:

- Compute $u^-_{1/2} \in \mathcal{M}$ as the solution at time $t_0 + \frac{1}{2}\Delta t$ of

$$\left\langle \delta u \,\middle|\, \mathrm{i}\frac{\partial}{\partial t} - T \,\middle|\, u \right\rangle = 0 \quad \forall \delta u \in \mathcal{T}_u\mathcal{M}, \tag{46}$$

  with initial value $u(t_0) = u_0$.
- Compute $u^+_{1/2} \in \mathcal{M}$ as the solution at time $t_0 + \Delta t$ of

$$\left\langle \delta u \,\middle|\, \mathrm{i}\frac{\partial}{\partial t} - V \,\middle|\, u \right\rangle = 0 \quad \forall \delta u \in \mathcal{T}_u\mathcal{M}, \tag{47}$$

  with initial value $u(t_0) = u^-_{1/2}$.
- Compute $u_1 \in \mathcal{M}$ as the solution at time $t_0 + \Delta t$ of (46) with initial value $u(t_0 + 1/2\Delta t) = u^+_{1/2}$.

Note that with the gaugeing (8), this is equivalent to using the usual second order, symmetric operator splitting (commonly known as *Strang splitting*) on the equations (9)–(10) [23]. Thus, since $Tu \in \mathcal{T}_u\mathcal{M}$ for $u \in \mathcal{M} \cap H^2$, the two steps (46) are equivalent to solving the linear Schrödinger equations

$$\mathrm{i}\frac{\partial u}{\partial t} = Tu \tag{48}$$

on the respective domains. If the initial function is chosen in $\mathcal{M}$, (48) decouples into a set of single particle, linear Schrödinger equations:

$$\frac{da_J}{dt} = 0, \quad \forall J, \tag{49}$$

$$\mathrm{i}\frac{\partial \phi_j}{\partial t} = T\phi_j, \quad j = 1, \dots, N. \tag{50}$$

The step (47) amounts to the solution of the nonlinear system

$$\mathrm{i}\frac{da}{dt} = \mathcal{A}_V(\phi)a, \qquad \mathrm{i}\frac{\partial \phi}{\partial t} = \mathcal{B}_V(a, \phi). \tag{51}$$

Motivated by the observation that the variational splitting defined above is equivalent to a splitting of the vector field defining (9)–(10), we define

$$\hat{T} := -\mathrm{i}(0, T)^T, \qquad \hat{V} := -\mathrm{i}(\mathcal{A}_V, \mathcal{B}_V), \qquad \hat{H} := \hat{T} + \hat{V}. \tag{52}$$

Advantages of this splitting have been described in [21] and [28], for instance. Convergence for bounded potentials was also demonstrated in [28]. For nonlinear Schrödinger and Schrödinger-Poisson equations, the method was analyzed in [27]. Our analysis in Section 4.2 uses similar techniques, where in particular the calculus of *Lie derivatives* is employed. This is presented in Section 4.3.

4.2. **Convergence Proof for Variational Splitting.** Our proof of the convergence of variational splitting as stated in Theorem 1.2 proceeds as follows: Denote by u the exact solution of the MCTDHF equations (9)–(10), and by $(u_0, u_1, \dots)$ the approximate solution resulting from variational splitting.

Step 1 *First, stability in the H^1 norm is shown: If for some constant $M_1 > 0$*

$$\|u\|_{H^1} \le M_1, \qquad \|v\|_{H^1} \le M_1, \tag{53}$$

then we have

$$\|\mathcal{S}_{\Delta t}(u) - \mathcal{S}_{\Delta t}(v)\|_{H^1} \le \mathrm{e}^{c_1 \Delta t} \|u - v\|_{H^1}, \tag{54}$$

with a constant $c_1 = c_1(M_1)$.

Step 2 *We then estimate the local error in H^1. Recall that the exact solution resulting from* (9)–(10) *is denoted by $u(t)$. Let $u \in H^2$ and for some constant $M_2 > 0$,*

$$\|u\|_{H^2} \le M_2, \tag{55}$$

then

$$\|\mathcal{S}_{\Delta t}(u_0) - u(\Delta t)\|_{H^1} \le c_2 (\Delta t)^2, \tag{56}$$

with a constant $c_2 = c_2(M_2)$. In this argument, a bound for the commutator $\|[\hat{T}, \hat{V}](u)\|_{H^1} = \|[\mathrm{i}T, \mathrm{i}\mathcal{B}_V](u)\|_{H^1}$ is used. This depends on the H^2-norm of u.

Step 3 *Combining stability* (54) *and consistency* (56) *in H^1, the standard argument referred to as* Lady Windermere's fan *in* [15, Section II.3] *then yields convergence in H^1,*

$$\|u_n - u(t_n)\|_{H^1} \le \mathrm{const.} \Delta t, \qquad \textit{for } t_n = n \Delta t. \tag{57}$$

Step 4 *Boundedness of the numerical solution in H^1,*

$$\|u_n\|_{H^1} \le \mathrm{const.}, \tag{58}$$

now follows inductively from the error bound (57).

Step 5 *Next, stability in L^2 is investigated. It is found that*

$$\|\mathcal{S}_{\Delta t}(u) - \mathcal{S}_{\Delta t}(v)\|_{L^2} \le \mathrm{e}^{c_3 \Delta t} \|u - v\|_{L^2}, \tag{59}$$

with a constant $c_3 = c_3(M_1)$.

Step 6 *Then, the local error in L^2 is estimated. To this end, the L^2-norm of the double commutator $\|[\hat{T}, [\hat{T}, \hat{V}]](u)\|_{L^2} = \|[\mathrm{i}T, [\mathrm{i}T, \mathrm{i}\mathcal{B}_V]](u)\|_{L^2}$ is estimated. The bound depends on $M_3 = \|u\|_{H^3}$. From this it is concluded that*

$$\|\mathcal{S}_{\Delta t}(u_0) - u(\Delta t)\|_{L^2} \le c_4 (\Delta t)^3, \tag{60}$$

where $c_4 = c_4(M_3)$.

Step 7 *Since we had previously concluded that $\|u_n\|_{H^1}$ is bounded in* (58)*, the stability estimate* (59) *in conjunction with* (60) *now yields convergence:*

$$\|u_n - u(t_n)\|_{L^2} \le \mathrm{const.} (\Delta t)^2. \tag{61}$$

Step 8 *Finally we conclude that the numerical approximation u_n is in H^2 by showing boundedness of $u^+_{1/2}$.*

4.3. **The Calculus of Lie Derivatives.** For our convergence analysis, we are going to use the calculus of Lie derivatives to derive estimates for the local error of the splitting method from Section 4.1, see also [27], [14].

For a (nonlinear) vector field F, we denote by φ_F^t the flow of the differential equation $\dot{\psi} = F(\psi)$, so that $\varphi_F^t(\psi_0)$ is the solution at time t of the differential equation $\dot{\psi} = F(\psi)$, $\psi(0) = \psi_0$. If G is another vector field, the *Lie derivative* D_F is now defined by

$$(D_F G)(\psi) = \frac{d}{dt}\bigg|_{t=0} G(\varphi_F^t(\psi)) = G'(\psi)F(\psi) \tag{62}$$

for a vector field G on H^1 and $\psi \in H^1$. We now define

$$\big(\exp(tD_F)G\big)(\psi) := G(\varphi_F^t(\psi)). \tag{63}$$

If G is the identity, the exact flow is thus reproduced as $\exp(tD_F)\mathrm{Id}(\psi) = \varphi_F^t(\psi)$. We have the following manipulation rules:

$$\frac{d}{dt}\exp(tD_F)G(\psi) = \left(D_F \exp(tD_F)G\right)(\psi) = \left(\exp(tD_F)D_F G\right)(\psi), \tag{64}$$

$$[D_F, D_G] = D_{[G,F]} \tag{65}$$

for the *commutator* $[D_F, D_G] := D_F D_G - D_G D_F$ of the Lie derivatives of two vector fields F and G.

4.4. **Commutator bounds.** In order to analyse the error of *variational splitting* [28] along the line of argument given in Section 4.2, we need to derive estimates for *commutators* of partial differential operators and the nonlinear operators in the right-hand sides of (9)–(10), see also [25].

By inspection of the derivation of the MCTDH(F) equations of motion [3], see also [25], we find that commutators of the nonlinear parts of (9)–(10) with the kinetic energy operators contain terms of the following forms:

For commutators with T, $[\hat{T}, \hat{V}] = [(0, -\mathrm{i}T)^T, -\mathrm{i}(\mathcal{A}_V, \mathcal{B}_V)^T] = (0, [\mathrm{i}\Delta, -\mathrm{i}\mathcal{B}_V])^T$:

$$\mathcal{C}_4(y) := \left\langle \phi_1(x) \left| \Delta_y \frac{1}{|x-y|} \right| \phi_2(x) \right\rangle_{L^2(x)} \phi_3(y) = \phi_1(y)\phi_2(y)\phi_3(y), \tag{66}$$

$$\mathcal{C}_5(y) := \left\langle \phi_1(x) \left| \Delta_x \frac{1}{|x-y|} \right| \phi_2(x) \right\rangle_{L^2(x)} \phi_3(y) = \phi_1(y)\phi_2(y)\phi_3(y), \tag{67}$$

$$\mathcal{C}_6(y) := \left\langle \phi_1(x) \left| \nabla_y \frac{1}{|x-y|} \right| \phi_2(x) \right\rangle_{L^2(x)} \nabla_y \phi_3(y), \tag{68}$$

$$\mathcal{C}_7(y) := \left\langle \phi_1(x) \left| \nabla_x \frac{1}{|x-y|} \right| \nabla_x \phi_2(x) \right\rangle_{L^2(x)} \phi_3(y), \tag{69}$$

Due to the antisymmetry expressed in the formulation (34), it is clear, however, that the contributions from $\mathcal{C}_4(y)$ and $\mathcal{C}_5(y)$ cancel, respectively. The other terms can be estimated using the techniques outlined in Section 3. We obtain the following bounds:

$$\|\mathcal{C}_6\|_{L^2} \leq \text{const.}\|\phi_1\|_{H^1}\|\phi_2\|_{H^1}\|\phi_3\|_{H^1}, \tag{70}$$

$$\|\mathcal{C}_7\|_{L^2} \leq \text{const.}\|\phi_1\|_{H^1}\|\phi_2\|_{H^2}\|\phi_3\|_{L^2}, \tag{71}$$

Finally, the convergence proof also requires to estimate the H^1 norms of the commutators.

We find that

$$\|\mathcal{C}_6\|_{H^1} \leq \text{const.}\|\phi_1\|_{H^1}\|\phi_2\|_{H^1}\|\phi_3\|_{H^2}, \tag{72}$$

$$\|\mathcal{C}_7\|_{H^1} \leq \text{const.}\|\phi_1\|_{H^1}\|\phi_2\|_{H^2}\|\phi_3\|_{H^1}. \tag{73}$$

Repeating the analogous derivations to compute the terms in the double commutator $[\hat{T},[\hat{T},\hat{V}]] = [(0,-\mathrm{i}T)^T,[(0,-\mathrm{i}T)^T,-\mathrm{i}(\mathcal{A}_V,\mathcal{B}_V)^T] = (0,[\mathrm{i}\Delta,[\mathrm{i}\Delta,-\mathrm{i}\mathcal{B}_V]])^T$ reveals that this contains the following terms:

$$\begin{aligned}
\mathcal{C}_{10}(y) &:= \left\langle \phi_1(x) \left| \Delta_y \nabla y \frac{1}{|x-y|} \right| \phi_2(x) \right\rangle_{L^2(x)} \nabla_y \phi_3(y) \\
&= (\nabla_y\phi_1(y))(\nabla_y\phi_2(y))\nabla_y\phi_3(y),
\end{aligned} \tag{74}$$

$$\begin{aligned}
\mathcal{C}_{11}(y) &:= \left\langle \phi_1(x) \left| \Delta_x \nabla y \frac{1}{|x-y|} \right| \phi_2(x) \right\rangle_{L^2(x)} \nabla_y \phi_3(y) \\
&= (\nabla_y\phi_1(y))(\nabla_y\phi_2(y))\nabla_y\phi_3(y),
\end{aligned} \tag{75}$$

$$\begin{aligned}
\mathcal{C}_{12}(y) &:= \left\langle \phi_1(x) \left| \Delta_y \frac{1}{|x-y|} \right| \phi_2(x) \right\rangle_{L^2(x)} \Delta_y \phi_3(y) \\
&= \phi_1(y)\phi_2(y)\Delta_y\phi_3(y),
\end{aligned} \tag{76}$$

$$\begin{aligned}
\mathcal{C}_{13}(y) &:= \left\langle \phi_1(x) \left| \nabla_y \nabla_x \frac{1}{|x-y|} \right| \nabla_x\phi_2(x) \right\rangle_{L^2(x)} \nabla_y \phi_3(y) \\
&= \phi_1(y)(\nabla_y\phi_2(y))(\nabla_y\phi_3(y)),
\end{aligned} \tag{77}$$

$$\begin{aligned}
\mathcal{C}_{14}(y) &:= \left\langle \phi_1(x) \left| \nabla_x \Delta_y \frac{1}{|x-y|} \right| \nabla_x\phi_2(x) \right\rangle_{L^2(x)} \phi_3(y) \\
&= (\nabla_y\phi_1(y))(\Delta_y\phi_2(y))\phi_3(y),
\end{aligned} \tag{78}$$

$$\begin{aligned}
\mathcal{C}_{15}(y) &:= \left\langle \phi_1(x) \left| \nabla_x^3 \frac{1}{|x-y|} \right| \nabla_x\phi_2(x) \right\rangle_{L^2(x)} \phi_3(y) \\
&= \mathcal{C}_{14}(y),
\end{aligned} \tag{79}$$

$$\begin{aligned}
\mathcal{C}_{16}(y) &:= \left\langle \phi_1(x) \left| \Delta_x \frac{1}{|x-y|} \right| \Delta_x\phi_2(x) \right\rangle_{L^2(x)} \phi_3(y) \\
&= \phi_1(y)(\Delta_y\phi_2(y))\phi_3(y).
\end{aligned} \tag{80}$$

Now taking into account the antisymmetry in (34), we find that the contributions from $\mathcal{C}_{10}(y)$, $\mathcal{C}_{11}(y)$, and $\mathcal{C}_{13}(y)$ vanish. Moreover, the other terms associated with $\mathcal{C}_{12}$, $\mathcal{C}_{14}$ and $\mathcal{C}_{16}$ actually take the forms

$$\hat{\mathcal{C}}_{12}(y) := \phi_1(y)(\phi_2(y)\Delta_y\phi_3(y) - (\Delta_y\phi_2(y))\phi_3(y)), \tag{81}$$

$$\hat{\mathcal{C}}_{14}(y) := (\nabla_y\phi_1(y))((\Delta_y\phi_2(y))\phi_3(y) - (\Delta_y\phi_3(y))\phi_2(y)), \tag{82}$$

$$\hat{\mathcal{C}}_{16}(y) := \phi_1(y)((\Delta_y\phi_2(y))\phi_3(y) - (\Delta_y\phi_3(y))\phi_2(y)). \tag{83}$$

This representation reveals that also the contributions from $\hat{\mathcal{C}}_{12}(y)$ and $\hat{\mathcal{C}}_{16}(y)$ cancel, as they appear in the same equation and are multiplied by the same prefactors. It only remains to estimate $\mathcal{C}_{14}$. It is easily seen that

$$\|\hat{\mathcal{C}}_{14}\|_{L^2} \leq \text{const.}\|\phi_1\|_{H^2}\|\phi_2\|_{H^3}\|\phi_3\|_{H^3}, \tag{84}$$

using (19).

4.5. **Proof details.** We now work out the details of the roadmap given in Section 4.2, using the estimates from Sections 3 and 4.4. Without restriction of generality, we let $t_0 = 0$.

Step 1 The substeps (46) amount to the solution of free Schrödinger equations (48), which are known to preserve the H^1-norm, see (22). Moreover, the coefficients a satisfy a system of ordinary differential equations with a skew-hermitian system matrix, whence the norm of a is preserved [25]. The substep (47) for each ϕ is equivalent to

$$\phi(0) \to \phi(0) - \mathrm{i}\int_0^{\Delta t} \mathcal{B}_V(a(s), \phi(s))\, ds,$$

cf. (43). Now, by (39) and the Gronwall lemma [16] it is clear that (54) holds.

Step 2 We denote by D_H, D_T and D_V the Lie derivatives defined by the vector fields $\hat{H}$, $\hat{T}$ and $\hat{V}$, respectively, see (52), leaving out for simplicity the 'hats' in the subscripts. For a shorter notation, we write for the vector containing the coefficients and the orbitals $\vec{u} := (a, \phi)^T$ (recall that $\phi = (\phi_j)$ is the vector of single-particle functions). We recast the exact solution $\vec{u}(t) = \exp(tD_H)\mathrm{Id}(\vec{u}(0))$ (for better readability we have replaced Δt by t) using a nonlinear version of the variation of constant formula (also known as *Gröbner-Alekseev-Lemma* [15]) twice,

$$\begin{aligned} \vec{u}(t) &= \exp(tD_H)\mathrm{Id}(\vec{u}(0)) = \exp(tD_T)\mathrm{Id}(\vec{u}(0)) + \cdots \\ &\quad + \int_0^t \exp((t-s)D_H) D_V \exp(sD_T)\mathrm{Id}(\vec{u}(0))\, ds \\ &= \exp(tD_T)\mathrm{Id}(\vec{u}(0)) + \cdots \\ &\quad + \int_0^t \exp((t-s)D_T) D_V \exp(sD_T)\mathrm{Id}(\vec{u}(0))\, ds + r_1, \end{aligned} \tag{85}$$

with the remainder term given by

$$\begin{aligned} r_1 \;:=\; & \int_0^t \int_0^{t-s} \exp\left((t-s-\sigma)D_H\right) \cdots \\ & \cdot D_V \exp(\sigma D_T) D_V \exp(sD_T)\mathrm{Id}(\vec{u}(0))\, d\sigma\, ds. \end{aligned} \tag{86}$$

On the other hand, we observe that the numerical solution can be recast as

$$\vec{u}_t = \mathcal{S}_t \vec{u}(0) = \exp\left(\frac{1}{2}tD_T\right) \exp\left(tD_V\right) \exp\left(\frac{1}{2}tD_T\right) \mathrm{Id}(\vec{u}(0)), \tag{87}$$

whence by Taylor expansion of $\exp(tD_V)$

$$\vec{u}_t = \exp\left(tD_T\right)\mathrm{Id}(\vec{u}(0)) + t\exp\left(\frac{1}{2}tD_T\right) D_V \exp\left(\frac{1}{2}tD_T\right)\mathrm{Id}(\vec{u}(0)) + r_2 \tag{88}$$

with

$$r_2 = t^2 \int_0^1 (1-\theta) \exp\left(\frac{1}{2}tD_T\right) \exp\left(\theta t D_V\right) D_V^2 \exp\left(\frac{1}{2}tD_T\right) \mathrm{Id}(\vec{u}(0))\, d\theta.$$

Subtracting (85) from (88), we thus obtain

$$\vec{u}_t - \vec{u}(t) = t\exp\left(\frac{1}{2}tD_T\right)D_V\exp\left(\frac{1}{2}tD_T\right)\mathrm{Id}(\vec{u}(0)) - \cdots$$
$$- \int_0^t \exp\left((t-s)D_T\right)D_V\exp\left(sD_T\right)\mathrm{Id}(\vec{u}(0))\,ds + r_2 - r_1. \tag{89}$$

Thus, the principal error term corresponds with the quadrature error of the midpoint rule applied to the integral over $[0,t]$ of the function

$$f(s) := \exp\left((t-s)D_T\right)D_V\exp(sD_T)\mathrm{Id}(\vec{u}(0)). \tag{90}$$

The quadrature error can be written in *first order Peano form* as

$$tf(t/2) - \int_0^t f(s)\,ds = t^2\int_0^1 \kappa_1(\sigma)f'(\sigma t)\,d\sigma,$$

with the scalar, bounded *Peano kernel* κ_1 of the midpoint rule [38]. We can now compute

$$\begin{aligned} f'(s) &= -\exp\left((t-s)D_T\right)[D_T,D_V]\exp\left(sD_T\right)\mathrm{Id}(\vec{u}(0)) \\ &= \exp\left((t-s)D_T\right)D_{[\hat{T},\hat{V}]}\exp\left(sD_T\right)\mathrm{Id}(\vec{u}(0)) \\ &= \exp\left(s\hat{T}\right)[\hat{T},\hat{V}]\left(\exp\left((t-s)\hat{T}\right)\vec{u}(0)\right). \end{aligned} \tag{91}$$

Now, by virtue of the commutator bounds derived in Section 4.4, it is clear that

$$\left\|tf(t/2) - \int_0^t f(s)\,ds\right\|_{H^1} \le c_2 t^2 \tag{92}$$

where c_2 depends on $\|\vec{u}\|_{H^2}$ (recall that $\|a\|$ is preserved). It remains to derive a bound for $\|r_2 - r_1\|_{H^1} \le \|r_1\|_{H^1} + \|r_2\|_{H^1}$. Setting $\rho := t - s - \sigma$, we observe that

$$\begin{aligned} &\exp\left(\rho D_H\right)D_V\exp(\sigma D_T)D_V\exp(sD_T)\mathrm{Id}(\vec{u}(0)) \\ &\quad = \exp\left(s\hat{T}\right)\hat{V}'\left(\exp\left(\sigma\hat{T}\right)\vec{u}(\rho)\right)\exp\left(\sigma\hat{T}\right)\hat{V}(\vec{u}(\rho)), \\ &\exp\left(\frac{1}{2}tD_T\right)\exp\left(\theta tD_V\right)D_V^2\exp\left(\frac{1}{2}tD_T\right)\mathrm{Id}(\vec{u}(0)) \\ &\quad = \exp\left(\frac{1}{2}t\hat{T}\right)\hat{V}'(\eta)\hat{V}(\eta), \end{aligned}$$

where

$$\eta := \exp\left(\theta t\hat{V}(\varphi)\right)\varphi, \qquad \varphi := \exp\left(t\hat{T}\right)\vec{u}(0),$$

briefly denoting by $\exp\left(t\hat{V}(\varphi)\right)\varphi$ the flow of the subproblem (51) with initial value φ. Analogously to the proof of (54) (see **Step 1** of this proof) we conclude that

$$\|\eta\|_{H^1} \le \exp(\mathcal{C}t)\|\vec{u}(0)\|_{H^1}.$$

Finally, with the bounds

$$\|\hat{V}(\vec{u})\|_{H^1} \le \mathcal{C}_1(\|\vec{u}\|_{H^1}), \qquad \|\hat{V}'(\vec{u})\vec{u}^*\|_{H^1} \le \mathcal{C}_2(\|\vec{u}\|_{H^1}, \|\vec{u}^*\|_{H^1}), \tag{93}$$

with constants $\mathcal{C}_1,\ \mathcal{C}_2$ depending on the H^1-norms of $\vec{u},\ \vec{u}^*$ (in the sense of the definition (31)), we can conclude

$$\|r_1 - r_2\|_{H^1} \le \|r_1\|_{H^1} + \|r_2\|_{H^1} \le \mathcal{C}t^2, \tag{94}$$

with a constant depending on the H^1-norm of $\vec{u}$.

Step 3 There is nothing to show, noting *Lady Windermere's fan* [15].

Step 4 Follows inductively from (57).

Step 5 This is concluded analogously as **Step 1**, noting (21), (37), (38).

Step 6 We revisit the error representation (89). We now write the principal error term in *second order Peano form* [38]

$$tf(t/2) - \int_0^t f(s)\,ds = t^3 \int_0^1 \kappa_2(\sigma) f''(\sigma t)\,d\sigma,$$

with the scalar, bounded *Peano kernel* κ_2 of the midpoint rule. Rearranging, it follows

$$\begin{aligned} f''(s) &= -\exp\left((t-s)D_T\right)[D_T,[D_T,D_V]]\exp(sD_T)\mathrm{Id}(\vec{u}(0)) \\ &= \exp\left((t-s)D_T\right) D_{[\hat{T},[\hat{T},\hat{V}]]}\exp(sD_T)\mathrm{Id}(\vec{u}(0)) \\ &= \exp(s\hat{T})[\hat{T},[\hat{T},\hat{V}]]\left(\exp\left((t-s)\hat{T}\right)\vec{u}(0)\right). \end{aligned} \tag{95}$$

Thus, by the estimates derived in Section 4.4, it is clear that

$$\left\| tf(t/2) - \int_0^t f(s)\,ds \right\|_{L^2} \le \mathcal{C}t^3 \tag{96}$$

where $\mathcal{C}$ depends on $\|\vec{u}\|_{H^3}$. Finally, we estimate the remainder terms. Defining

$$g(s,\sigma) := \exp\left((t-s-\sigma)D_T\right) D_V \exp\left(\sigma D_T\right) D_V \exp(sD_T)\mathrm{Id}(\vec{u}(0)),$$

we can write

$$r_2 - r_1 = \frac{t^2}{2} g(t/2,0) - \int_0^t \int_0^{t-s} g(s,\sigma)\,d\sigma\,ds + \tilde{r}_2 - \tilde{r}_1. \tag{97}$$

Similarly as in **Step 2**, the remainders satisfy

$$\|\tilde{r}_1\|_{L^2} + \|\tilde{r}_2\|_{L^2} \le \tilde{\mathcal{C}}t^3,$$

where $\tilde{\mathcal{C}}$ depends on $\|\vec{u}\|_{H^1}$. The other terms in (97) represent the (local) error of a first-order, two-dimensional quadrature formula, and hence

$$\begin{aligned} &\left\| \frac{t^2}{2} g(t/2,0) - \int_0^t \int_0^{t-s} g(s,\sigma)\,d\sigma\,ds \right\|_{L^2} \\ &\quad \le \text{const.}\,t^3 \left(\max \left\| \frac{\partial g}{\partial s} \right\|_{L^2} + \max \left\| \frac{\partial g}{\partial \sigma} \right\|_{L^2} \right), \end{aligned} \tag{98}$$

with the maxima taken over the triangle defined by $0 \le s \le t,\ 0 \le \sigma \le t-s$. Computing

$$\begin{aligned} \frac{\partial g}{\partial s}(s,\sigma) &= \exp\left((t-s-\sigma)D_T\right) D_{[\hat{T},\hat{V}]} \exp\left(\sigma D_T\right) D_V \exp(sD_T)\mathrm{Id}(\vec{u}(0)) + \cdots \\ &\quad + \exp\left((t-s-\sigma)D_T\right) D_V \exp\left(\sigma D_T\right) D_{[\hat{T},\hat{V}]} \exp(sD_T)\mathrm{Id}(\vec{u}(0)) \\ \frac{\partial g}{\partial \sigma}(s,\sigma) &= \exp\left((t-s-\sigma)D_T\right) D_{[\hat{T},\hat{V}]} \exp\left(\sigma D_T\right) D_V \exp(sD_T)\mathrm{Id}(\vec{u}(0)) \end{aligned}$$

we realize that these partial derivatives only contain $\hat{V}$ and $[\hat{T}, \hat{V}]$ together with their derivatives, whose L^2-norms can be estimated in terms of $\|\vec{u}\|_{H^2}$ by virtue of (93). Altogether, we obtain

$$\|r_2 - r_1\|_{L^2} \leq \mathcal{C} t^3,$$

where the constant $\mathcal{C}$ depends on $\|\vec{u}\|_{H^2}$. Recalling (89), we obtain (60).

Step 7 Uses the same standard argument as in **Step 3**.

Step 8 We note that the split-steps (46) preserve the H^2-norm due to (23), and thus we only need a bound for the step (47). Since the norm of a is preserved in any case, we write this step as $\phi^-_{1/2} \mapsto \phi^+_{1/2}$, and it is found that

$$\|\phi^+_{1/2}(t)\|_{H^2} \leq \|\phi^-_{1/2}\|_{H^2} + \text{const.} \int_0^t (\|\phi^-_{1/2}\|_{H^2} + \|\phi^+_{1/2}(s)\|_{H^2})\, ds, \tag{99}$$

whence by the Gronwall lemma [5] it follows that

$$\|\phi^+_{1/2}(t)\|_{H^2} \leq \exp(Ct)\|\phi^-_{1/2}\|_{H^2},$$

with a constant $C = C(\|\phi^-_{1/2}\|_{L^2}, \|\phi^-_{1/2}\|_{H^1})$.

5. Conclusions and Outlook

In this paper, we have analyzed the regularity of the approximation to the solution of the time-dependent Schrödinger equation defined by the multi-configuration time-dependent Hartree-Fock method, and the convergence of time integration based on splitting of the vector field.

The H^2 regularity established in Theorem 1.1 has important consequences for the approximation properties of the MCTDHF approach. According to [29, Theorem 4.1], at least for bounded potentials the error of the approximation to the exact wave function is — for sufficiently short time intervals — of the same order of magnitude as the error of the best approximation in the approximation manifold. This result requires H^2 regularity of the approximate wave function.

The regularity is also needed to ensure good performance of numerical methods used to solve the MCTDHF equations, both for space discretization and for the variational splitting integrator of [28] for the discretization in time. The convergence of the latter in the present setting of the electronic Schrödinger equation with Coulomb interaction was investigated in Section 4.2.

We were able to establish the convergence of this time integrator in Theorem 1.2. A first order error bound was derived in the H^1-norm, while the classical convergence order two was shown in L^2. Thus, it is possible to efficiently treat the single particle part and the particle-particle interactions in the Hamiltonian separately, using different suitable time integrators and different step sizes, see [21, 23, 28].

Appendix A. Nuclear attractive potential

We indicate necessary extensions to incorporate nuclear attraction into the kinetic energy operator T, such that

$$T^{(k)} := -\frac{1}{2}\Delta + U(x^{(k)}) = -\frac{1}{2}\Delta - \frac{1}{|x^{(k)}|}, \tag{100}$$

where without restriction of generality we have set $Z := 1$.

For the extension of the analysis of Theorem 1.1, we note that (100) still generates a strongly continuous semigroup on H^2, since $1/|x| \ll \Delta$, see [18, p. 303]. Thus the proposition remains valid.
The extension of Theorem 1.2 is technically involved and is not treated here.

Appendix B. Drift term

Finally, we describe necessary extensions to incorporate the drift term modeling the laser pulse into T, such that

$$T^{(k)} := \frac{1}{2}\left(-\mathrm{i}\nabla^{(k)} - A(t)\right)^2. \tag{101}$$

For the extension of the analysis of Theorem 1.1, we note that (101) still generates a strongly continuous semigroup on H^2, since A is bounded and $\nabla \ll \Delta$, see [35, Theorem X.22]. Thus, the proposition of Theorem 1.1 remains valid.
For the analysis of variational splitting, we additionally need the following commutator bounds.
Terms in commutators with first partial derivatives, $[\nabla, -\mathrm{i}\mathcal{B}_V]$:

$$\mathcal{C}_1(y) := \left\langle \phi_1(x) \left| \nabla_y \frac{1}{|x-y|} \right| \phi_2(x) \right\rangle_{L^2(x)} \phi_3(y), \tag{102}$$

$$\mathcal{C}_2(y) := \left\langle \phi_1(x) \left| \nabla_x \frac{1}{|x-y|} \right| \phi_2(x) \right\rangle_{L^2(x)} \phi_3(y), \tag{103}$$

(104)

These are estimated as follows:

$$\|\mathcal{C}_1\|_{L^2} \leq \text{const.}\|\phi_1\|_{H^1}\|\phi_2\|_{H^1}\|\phi_3\|_{L^2}, \tag{105}$$

$$\|\mathcal{C}_2\|_{L^2} \leq \text{const.}\|\phi_1\|_{H^1}\|\phi_2\|_{H^1}\|\phi_3\|_{L^2}, \tag{106}$$

$$\|\mathcal{C}_1\|_{H^1} \leq \text{const.}\|\phi_1\|_{H^1}\|\phi_2\|_{H^1}\|\phi_3\|_{H^1}, \tag{107}$$

$$\|\mathcal{C}_2\|_{H^1} \leq \text{const.}\|\phi_1\|_{H^1}\|\phi_2\|_{H^1}\|\phi_3\|_{H^1}. \tag{108}$$

Finally, a close inspection of the earlier arguments reveals that for the double commutator, the expression $[\nabla, [\hat{T}, \hat{V}]]$ does not contain any new terms due to cancellations taking into account the antisymmetry.
Thus, the assertion of Theorem 1.2 remains valid.

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