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The Variational Splitting Method for the Multi-Configuration Time-Dependent Hartree-Fock Equations for Atoms [1] [2]

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Abstract: We discuss the numerical approximation of the solution to the multi-configuration time-dependent Hartree-Fock (MCTDHF) equations in quantum dynamics. The associated 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 extend the analysis of the convergence of a time integrator based on splitting of the vector field for systems of unbound fermions to the case where a nuclear attractive potential is present. First order convergence in the H^1 norm and second order convergence in L^2 are established. The analysis applies to electronic states whose density vanishes at the nucleus.

Keywords: MCTDHF method, electronic Schrödinger equation, time integration, splitting methods

Mathematics Subject Classification: 65M12, 81V45

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Introduction

This paper deals with the multi-configuration time-dependent Hartree-Fock (MCTDHF) approach [3, 21] to the approximate solution of the time-dependent electronic Schrödinger equation

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

where the wave function $\psi = \psi\left(x^{(1)}, \ldots, x^{(f)}, t\right)$ 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

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

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where

$$U(x) := -\frac{Z}{|x|} = -\frac{Z}{\sqrt{x_1^2 + x_2^2 + x_3^2}}, \quad Z \in \mathbb{N}, \tag{3}$$

$$V(x-y) := \frac{1}{|x-y|} = \frac{1}{\sqrt{(x_1-y_1)^2 + (x_2-y_2)^2 + (x_3-y_3)^2}}, \tag{4}$$

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, and U is associated with the nuclear attractive force, where $Z > f - 1$ describes the nuclear charge [13].

The applications that motivate this research are given by the study of ultrafast laser pulses in photonics [3, 21], where the kinetic part of the Hamiltonian additionally depends on a time-dependent drift term modeling the laser, such that

$$T^{(k)} := \frac{1}{2}\left(-\mathrm{i}\nabla^{(k)} + A(t)\right)^2 + U\left(x^{(k)}\right). \tag{5}$$

The existence of regular solutions to the MCTDHF equations for (2) with (5) was established in [10]. Also, the numerical approximation for $T^{(k)} := -\frac{1}{2}\Delta^{(k)}$ was discussed in this reference. The modifications necessary for the numerical treatment of $T^{(k)} := \frac{1}{2}\left(-\mathrm{i}\nabla^{(k)} + A(t)\right)^2$ are straightforward [10]. The aim of the present paper is to extend the convergence result for *variational splitting* time integration [10, 14] to systems (5) subject to the nuclear attractive potential U (3). Additionally, the drift term present in (5) will also be treated. Our analysis applies to electrons whose density vanishes at the nucleus, see for instance [17], where a laser pulse is used to realize localized Bohr-like wave packets. Generally, for a point-like nucleus as considered here, this situation is realized for any of the electronic orbitals in the atom with the exception of the s-orbitals. Due to their vanishing angular momentum, only the probability density of the latter to be found at the position of the nucleus does not vanish [16].

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 [3, 21], which is closely related to the MCTDH method in quantum molecular dynamics [2, 18].

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* [12]. The Dirac–Frenkel time-dependent variational principle [4, 5] 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. A detailed exposition of the theory and numerical realization of this and related variational approximations is given in [15].

In Section 3, we study the approximation of the MCTDHF equations by time semi-discretization employing an operator splitting introduced in [14]. It is shown that for a symmetric, second-order splitting, first order convergence holds in H^1 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 $x = \left(x^{(1)}, \dots, x^{(f)}\right)$,

$$\begin{aligned}\psi(x,t) \quad &\approx \quad u(x,t) = \sum_J a_J(t)\, \Phi_J(x,t) \\ &= \sum_{(j_1,\dots,j_f)} a_{j_1,\dots,j_f}(t)\, \phi_{j_1}\left(x^{(1)},t\right)\cdots \phi_{j_f}\left(x^{(f)},t\right). \end{aligned} \tag{6}$$

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 complex-valued *single-particle functions* $\phi_{j_k}\left(x^{(k)}, t\right)$ (also referred to as *orbitals*) depend on the coordinates $x^{(k)}$ of a single particle and on time t. Since electrons are indistinguishable, the same N is used for each degree of freedom. 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. To accommodate for our assumption that the electronic wave function vanishes at the nucleus, we also assume that $u(x,t) = 0$ if $x_j = 0$ for any j.

The Dirac–Frenkel variational principle [4, 5] is used to derive differential equations for the coefficients a_J and the single-particle functions ϕ_j in (6). Thus, for u in the manifold $\mathcal{M}$ of ansatz functions (6), we require

$$\left\langle \delta u \,\middle|\, \mathrm{i}\frac{\partial u}{\partial t} - Hu \right\rangle = 0, \tag{7}$$

where δu varies in the tangent space $\mathcal{T}_u\mathcal{M}$ of $\mathcal{M}$ at u. $\langle\cdot|\cdot\rangle$ denotes the standard inner product in the function space L^2, i.e.

$$\langle f|g\rangle = \int_{\mathbb{R}^{3f}} \overline{f(x)}g(x)\,dx.$$

This variational approximation procedure is discussed in its abstract form in [9]. In the present paper, we are going to discuss the numerical time integration of the MCTDHF equations by splitting methods.

Using the Dirac–Frenkel principle [4, 5] and imposing additional orthogonality constraints in $L^2(\mathbb{R}^3)$ on the single-particle functions $\phi_j(x,t)$,

$$\left\langle \phi_j \middle| \phi_k \right\rangle = \delta_{j,k}, \quad j,k = 1,\dots,N, \quad t \ge 0, \tag{8}$$

$$\left\langle \phi_j \,\middle|\, \frac{\partial \phi_k}{\partial t} \right\rangle = -\mathrm{i}\left\langle \phi_j \,|\, T \,|\, \phi_k \right\rangle, \quad j,k = 1,\dots,N, \quad t \ge 0, \tag{9}$$

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 [2, 18] under the implicit assumption that a sufficiently regular solution exists:

$$\mathrm{i}\,\frac{da_J}{dt} \quad = \quad \sum_K \langle \Phi_J|V|\Phi_K\rangle\, a_K =: \mathcal{A}_V(\phi)a, \quad \forall J, \tag{10}$$

$$\begin{aligned}\mathrm{i}\,\frac{\partial \phi_j}{\partial t} \quad &= \quad T\phi_j + (1-P)\sum_{l=1}^{N}\sum_{m=1}^{N} \rho^{-1}_{j,m}\langle \psi_m|V|\psi_l\rangle \phi_l \\ &=: \quad T\phi + \mathcal{B}_V(a,\phi), \quad j = 1,\dots,N,\end{aligned} \tag{11}$$

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

$$\psi_j \quad := \quad \langle \phi_j \,|\, u\rangle, \quad j = 1,\dots,N. \tag{12}$$

The inner products $\langle\psi_m|V|\psi_l\rangle$ are over all variables except one (the arguments $x^{(2)},\ldots,x^{(f)}$ of $\psi_m,\ \psi_l$), and P is the orthogonal projector onto the space spanned by $\phi_1,\ldots,\phi_N$,

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

Finally,

$$\rho_{j,l}:=\langle\psi_j|\psi_l\rangle \tag{13}$$

denotes the *density matrix* which is assumed to be nonsingular[4]. This assumption, together with the orthogonality constraints (8) implies also that $\phi_j(0)=0$ for every $j=1,\ldots,N$. To see this, we compute

$$0=\langle u(0,x_2,\ldots,x_f)\,|\psi_j(x_2,\ldots,x_f)\rangle \quad = \quad \sum_{k=1}^{N}\rho_{k,j}\phi_k(0), \quad j=1,\ldots,N.$$

Under the assumption of invertibility of ρ, all the orbitals vanish at 0.
The problem formulation based on (9) 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 (10) and (11), we will analyze the convergence of a time integrator based on splitting of the vector field [14]. The convergence result can be formulated in the following theorem:

Theorem 1.1 *Consider the numerical approximation of* (10)–(11) *given by time semidiscretization with the variational splitting method from* Section 3.1, $u_n\mapsto u_{n+1}=\mathcal{S}_{\Delta t}u_n,\ n=0,1,\ldots.$ *Then the convergence estimates*

$$\begin{aligned}\|u_n-u(t_n)\|_{H^1} &\le \text{const.}\Delta t, \qquad \textit{for } t_n=n\Delta t, & (14)\\ \|u_n-u(t_n)\|_{L^2} &\le \text{const.}(\Delta t)^2, & (15)\end{aligned}$$

hold if the exact solution satisfies $u\in H^3$.

This result extends the convergence analysis for systems of free electrons interacting by Coulomb force in [10]. In the unbound situation, only a regularity $u\in H^2$ is required for the estimates (14) and (15).

2 Preliminaries

For our convergence analysis of variational splitting, we are going to use an extension of Hardy's inequality, see also [20]. This is based on the following inequality [6]:
Let f be an integrable, nonnegative real function, $f\not\equiv 0$,

$$F(t):=\int_0^t f(\tau)\,d\tau,$$

and $r>1$. Then for $p>1$,

$$\int_0^\infty \frac{1}{t^r}F^p(t)\,dt<\left(\frac{p}{r-1}\right)^p\int_0^\infty\frac{1}{t^r}(tf(t))^p\,dt. \tag{16}$$

Note that (16) implies the classical Hardy inequality in $\mathbb{R}^3$ for $p=r=2$ [7]. We thereby obtain

[4]The choice of the initial condition such that ρ is nonsingular ensures that this holds at least for small t. [1, 19] gives a criterion which ensures invertibility of ρ for all t in the spatially discrete case or on bounded domains.

Theorem 2.1 *Let $u \in H^2$ with $u(x) = 0$. Then*

$$\int_{\mathbb{R}^3} \frac{|u(y)|^2}{|x-y|^4} dy \le \mathcal{C}, \quad \mathcal{C} = \mathcal{C}(\|u\|_{H^2}). \tag{17}$$

Proof: For the proof, we transform (17) to polar coordinates with center x and compute

$$\begin{aligned}
\int_{\mathbb{R}^3} \frac{|u(y)|^2}{|y-x|^4}\, dy &= \int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \frac{|u(\rho,\varphi,\theta)|^2}{\rho^2} \sin(\theta)\, d\rho\, d\theta\, d\varphi \\
&\le 4\int_0^{2\pi}\int_0^{\pi}\int_0^{\infty} \left|\frac{\partial u(\rho,\varphi,\theta)}{\partial \rho}\right|^2 \sin(\theta)\, d\rho\, d\theta\, d\varphi \\
&\le 4\int_{\mathbb{R}^3} \frac{|\nabla u(y)|^2}{|x-y|^2}\, dy \\
&\le \mathcal{C}(\|u\|_{H^2}),
\end{aligned}$$

where the last estimate uses the classical Hardy inequality [6, 7]. □

3 Analysis of Variational Splitting

3.1 Variational Splitting

It has been suggested in [14] for a Hamiltonian $H = T + V$ as in (2) to use splitting methods to separate the computations in (10)–(11) 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

$$\left\langle \delta u \left| \mathrm{i}\frac{\partial}{\partial t} - T \right| u \right\rangle = 0 \quad \forall \delta u \in \mathcal{T}_u\mathcal{M}, \tag{18}$$

  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

$$\left\langle \delta u \left| \mathrm{i}\frac{\partial}{\partial t} - V \right| u \right\rangle = 0 \quad \forall \delta u \in \mathcal{T}_u\mathcal{M}, \tag{19}$$

  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 (18) with initial value $u(t_0 + 1/2\Delta t) = u^+_{1/2}$.

Note that with the gaugeing (9), this is equivalent to using the usual second-order, symmetric operator splitting (commonly known as *Strang splitting*) on the equations (10)–(11) [8]. Thus, since obviously $Tu \in \mathcal{T}_u\mathcal{M}$ for $u \in \mathcal{M} \cap H^2$ [11], the two steps (18) are equivalent to solving the linear Schrödinger equations

$$\mathrm{i}\frac{\partial u}{\partial t} = Tu \tag{20}$$

on the respective domains. If the initial function is chosen in $\mathcal{M}$, (20) decouples into a set of single particle, linear Schrödinger equations:

$$\frac{da_J}{dt} = 0, \quad \forall J, \tag{21}$$

$$\mathrm{i}\frac{\partial \phi_j}{\partial t} = T\phi_j, \quad j = 1, \ldots, N. \tag{22}$$

The step (19) amounts to the solution of the nonlinear system

$$\mathrm{i}\dot{a} = \mathcal{A}_V(\phi)a, \qquad \mathrm{i}\frac{\partial \phi}{\partial t} = \mathcal{B}_V(a, \phi). \tag{23}$$

Motivated by the observation that the variational splitting defined above is equivalent to a splitting of the vector field defining (10)–(11), we define

$$\hat{T} := -\mathrm{i}(0, T)^T, \qquad \hat{V} := -\mathrm{i}(\mathcal{A}_V, \mathcal{B}_V)^T, \qquad \hat{H} := \hat{T} + \hat{V}. \tag{24}$$

Advantages of this splitting have been described in [14], where convergence for bounded potentials was also demonstrated. For MCTDHF for gases of unbound fermions, where $T^{(k)} = -\frac{1}{2}\Delta^{(k)}$, the method was analyzed in [10]. Our analysis in Section 3.2 uses the same techniques. In particular, the estimates for the local error of the time integrator are given in terms of (iterated) *commutators* of $\hat{T}$ and $\hat{V}$. In the present paper, we focus on estimating the commutators with the single-particle operators T from (5), while the reader is referred to [10] for details of the convergence proof. The new estimates are derived in Section 3.3.

As the norms for the solution vectors we will use the following definitions: For coefficient vectors $a \in \mathbb{C}^m$, where $m := \binom{N}{f}$, we use the Euclidean norm

$$\|a\| = \Big(\sum_J |a_J|^2\Big)^{1/2}. \tag{25}$$

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

$$\|\phi\|_S = \max_j \|\phi_j\|_S, \tag{26}$$

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

$$\|(a, \phi)\|_S = \max\{\|a\|, \|\phi\|_S\}. \tag{27}$$

3.2 Convergence Proof for Variational Splitting

Our proof of the convergence of variational splitting as stated in Theorem 1.1 proceeds as follows, see also [10]: Denote by u the exact solution of the MCTDHF equations (10)–(11), and by $(u_0, u_1, \ldots)$ the approximate solution resulting from variational splitting.

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

$$\|u\|_{H^1} \le M_1, \qquad \|v\|_{H^1} \le M_1, \tag{28}$$

then we have

$$\|\mathcal{S}_{\Delta t}(u) - \mathcal{S}_{\Delta t}(v)\|_{H^1} \le \mathrm{e}^{c_1 \Delta t}\|u - v\|_{H^1}, \tag{29}$$

with a constant $c_1 = c_1(M_1)$. *This follows analogously as in* [10] *on noting that* $1/|x| \ll \Delta,\ \nabla \ll \Delta$ [7], *and thus the substeps* (18) *are propagated by a unitary semigroup of operators also in the case of* (5)[5].

Step 2 *We then estimate the local error in* H^1. *Recall that the exact solution resulting from* (10)–(11) *is denoted by* $u(t)$. *Let* $u \in H^3$ *and for some constant* $M_3 > 0$,

$$\|u\|_{H^3} \leq M_3, \tag{30}$$

then

$$\|\mathcal{S}_{\Delta t}(u_0) - u(\Delta t)\|_{H^1} \leq c_2(\Delta t)^2, \tag{31}$$

with a constant $c_2 = c_2(M_3)$. *In this argument, based on the theory of Lie derivatives and explained in detail in* [10], *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. We will show that this depends on the* H^3*-norm of* u *in* Section 3.3.

Step 3 *Combining stability* (29) *and consistency* (31) *in* H^1, *a standard argument then yields convergence in* H^1,

$$\|u_n - u(t_n)\|_{H^1} \leq C_1 \Delta t, \qquad \text{for } t_n = n\Delta t, \text{ with } C_1 = C_1(M_3). \tag{32}$$

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

$$\|u_n\|_{H^1} \leq \text{const.}, \tag{33}$$

now follows inductively from the error bound (32).

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

$$\|\mathcal{S}_{\Delta t}(u) - \mathcal{S}_{\Delta t}(v)\|_{L^2} \leq \mathrm{e}^{c_3 \Delta t} \|u - v\|_{L^2}, \tag{34}$$

with a constant $c_3 = c_3(M_1)$. *This follows from Hardy's inequality and the fact that* T *generates a unitary semigroup on* L^2 [10].

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. We will show in* Section 3.3 *that the bound depends on* $M_3 = \|u\|_{H^3}$. *From this it is concluded that*

$$\|\mathcal{S}_{\Delta t}(u_0) - u(\Delta t)\|_{L^2} \leq c_4(\Delta t)^3, \tag{35}$$

where $c_4 = c_4(M_3)$.

Step 7 *Since we had previously concluded that* $\|u_n\|_{H^1}$ *is bounded in* (33), *the stability estimate* (34) *in conjunction with* (35) *now yields convergence:*

$$\|u_n - u(t_n)\|_{L^2} \leq C_2(\Delta t)^2 \text{ with } C_2 = C_2(M_3). \tag{36}$$

Step 8 *Finally we conclude that the numerical approximation* u_n *is in* H^2 *by showing boundedness of* $u^+_{1/2}$. *This follows from a representation by the variation of constant formula, leading to*

$$\|u^+_{1/2}(t)\|_{H^2} \leq \|u^-_{1/2}\|_{H^2} + \text{const.} \int_0^t \left(\|u^-_{1/2}(s)\|_{H^2} + \|u^+_{1/2}(s)\|_{H^2} \right) ds, \tag{37}$$

and the Gronwall lemma. *Recall that the substeps* (18) *are norm-preserving, see* **Step 1**.

[5] In more detail, this means that the multiplication operator $\phi(x) \mapsto \frac{1}{|x|}\phi(x)$ and the differential operator $\phi(x) \mapsto \nabla\phi(x)$ are relatively bounded with respect to $\phi(x) \mapsto \Delta\phi(x)$, whence T generates a strongly continuous unitary semigroup on H^2 [7].

3.3 Commutator bounds

In order to analyse the error of *variational splitting* [14] along the line of argument given in Section 3.2, we need to derive estimates for *commutators* of the single particle operators $\hat{T}$ and the nonlinear operators in the right-hand sides of (10)–(11), see also [10].
It has been found [9, 10] that the right-hand side of the MCTDHF equations contains terms

$$\left\langle \phi_1(x) \left| \frac{1}{|x-y|} \right| \phi_2(x)\tilde{\phi}_2(y) - \tilde{\phi}_2(x)\phi_2(y) \right\rangle_{L^2(x)} =: \mathfrak{S}_1(y), \tag{38}$$

$$\left\langle \phi_1(x)\tilde{\phi}_1(y) \left| \frac{1}{|x-y|} \right| \phi_2(x)\tilde{\phi}_2(y) - \tilde{\phi}_2(x)\phi_2(y) \right\rangle_{L^2(x,y)} =: \mathfrak{S}_2, \tag{39}$$

accounting for the antisymmetry implied by the Pauli exclusion principle. $\phi_1,\ \tilde{\phi}_1,\ \phi_2,\ \tilde{\phi}_2$ are generic representations for any four of the orbitals $\phi_1, \dots, \phi_N$ in (6). It has been demonstrated in [10] that only terms associated with (38) appear in the commutators we need to estimate.
In the following, we list the terms appearing in the commutator $[-\mathrm{i}T, -\mathrm{i}\mathcal{B}_V]$ and double commutator $[-\mathrm{i}T, [-\mathrm{i}T, -\mathrm{i}\mathcal{B}_V]]$ and give estimates for them. We order the terms based on the three relevant contributions $\mathrm{i}\Delta,\ \nabla$, and $\mathrm{i}/|x|$ appearing in $T^{(k)}$ from (5) (for notational simplicity we set $Z := 1$ but remind the reader that in a stable atom, actually $Z > f-1$ [13]). Our observations are based on the computation of commutators of differential operators with the nonlinear vector field in [9]. For these considerations, we consider $\phi_1,\ \phi_2$ as compactly supported test functions in C^∞. This is sufficient for our analysis since the test functions are everywhere dense in H^m for all m.
Moreover, we use the following derivations necessary to incorporate a nuclear attractive potential (3) into the analysis: In this case, the commutators $[-\mathrm{i}U, -\mathrm{i}\mathcal{B}_V]$ are computed as follows:

$$\left[\frac{\mathrm{i}}{|x|}, -\mathrm{i}\mathcal{B}_V\right](u) = \frac{1}{|x|}\mathcal{B}_V(u) + \mathrm{i}\mathcal{B}_V{}'(u)\left(\frac{\mathrm{i}}{|x|}u\right), \tag{40}$$

with

$$\mathcal{B}_V{}'(u)\left(\frac{\mathrm{i}}{|x|}u\right) = \frac{d}{d\tau}\bigg|_{\tau=0} \mathcal{B}_V\left(\mathrm{e}^{\mathrm{i}/|x|\,\tau}u\right), \tag{41}$$

and $\left(\mathrm{e}^{\mathrm{i}/|x|\,\tau}u\right)$ is the flow of

$$\frac{\partial w}{\partial \tau} = \frac{\mathrm{i}}{|x|}w, \qquad w(0,x) = u(x).$$

Since $1/|x|$ is a real multiplication operator, it is symmetric and hence

$$\left\langle \mathrm{e}^{\mathrm{i}/|x|\,\tau}u \middle| V \middle| \mathrm{e}^{\mathrm{i}/|x|\,\tau}u \right\rangle = \left\langle u \middle| \mathrm{e}^{-\mathrm{i}/|x|\,\tau} V \mathrm{e}^{\mathrm{i}/|x|\,\tau}u \right\rangle.$$

Since $\mathrm{e}^{\mathrm{i}/|x|\,\tau}$ and $1/|x|$ commute, we conclude that τ does not appear in the right-hand side of (41), and hence

$$\mathrm{i}\mathcal{B}_V{}'(u)\left(\frac{\mathrm{i}}{|x|}u\right) = 0.$$

Consequently, $\left[\frac{\mathrm{i}}{|x|}, -\mathrm{i}\mathcal{B}_V\right]$ contains terms (already accounting for the antisymmetry) $\frac{1}{|y|}\mathfrak{S}_1(y)$.
By inspection of the derivation of the MCTDH(F) equations of motion [2, 9], we find that the commutator $[-\mathrm{i}T, -\mathrm{i}\mathcal{B}_V]$ contains the following terms, ordered by their origins from the contributions to the single-particle operator T:

- $[\mathrm{i}\Delta, -\mathrm{i}\mathcal{B}_V]$ contains terms of the following forms, after cancellations due to antisymmetry:

$$\mathcal{C}_1(y) := \left\langle \phi_1(x) \middle| \nabla_y \frac{1}{|x-y|} \middle| \phi_2(x) \right\rangle_{L^2(x)} \nabla_y \phi_3(y), \tag{42}$$

$$\mathcal{C}_2(y) := \left\langle \phi_1(x) \middle| \nabla_x \frac{1}{|x-y|} \middle| \nabla_x \phi_2(x) \right\rangle_{L^2(x)} \phi_3(y). \tag{43}$$

By the Hölder and Sobolev inequalities, these are estimated as follows using the same reasoning as in [10]: Noting that

$$\nabla_y \frac{1}{|x-y|} = \frac{1}{|x-y|^2} \overrightarrow{e}_{x-y}, \tag{44}$$

where $\overrightarrow{e}_{x-y}$ denotes the unit vector in direction $x-y$, we find by the Hardy inequality

$$\|\mathcal{C}_1\|_{L^2} \leq \text{const.} \|\phi_1\|_{H^1} \|\phi_2\|_{H^1} \|\phi_3\|_{H^1}, \tag{45}$$

$$\|\mathcal{C}_2\|_{L^2} \leq \text{const.} \|\phi_1\|_{H^1} \|\phi_2\|_{H^2} \|\phi_3\|_{L^2}. \tag{46}$$

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

$$\|\mathcal{C}_1\|_{H^1} \leq \text{const.} \|\phi_1\|_{H^1} \|\phi_2\|_{H^1} \|\phi_3\|_{H^2}, \tag{47}$$

$$\|\mathcal{C}_2\|_{H^1} \leq \text{const.} \|\phi_1\|_{H^1} \|\phi_2\|_{H^2} \|\phi_3\|_{H^1}. \tag{48}$$

- Commutators with first partial derivatives associated with the drift term, $[\nabla, -\mathrm{i}\mathcal{B}_V]$ contain the terms

$$\mathcal{C}_3(y) := \left\langle \phi_1(x) \middle| \nabla_y \frac{1}{|x-y|} \middle| \phi_2(x) \right\rangle_{L^2(x)} \phi_3(y), \tag{49}$$

$$\mathcal{C}_4(y) := \left\langle \phi_1(x) \middle| \nabla_x \frac{1}{|x-y|} \middle| \phi_2(x) \right\rangle_{L^2(x)} \phi_3(y). \tag{50}$$

These are estimated as follows:

$$\|\mathcal{C}_3\|_{L^2} \leq \text{const.} \|\phi_1\|_{H^1} \|\phi_2\|_{H^1} \|\phi_3\|_{L^2}, \tag{51}$$

$$\|\mathcal{C}_4\|_{L^2} \leq \text{const.} \|\phi_1\|_{H^1} \|\phi_2\|_{H^1} \|\phi_3\|_{L^2}, \tag{52}$$

$$\|\mathcal{C}_3\|_{H^1} \leq \text{const.} \|\phi_1\|_{H^1} \|\phi_2\|_{H^1} \|\phi_3\|_{H^1}, \tag{53}$$

$$\|\mathcal{C}_4\|_{H^1} \leq \text{const.} \|\phi_1\|_{H^1} \|\phi_2\|_{H^1} \|\phi_3\|_{H^1}. \tag{54}$$

- The commutator $\mathcal{C}_5 := \left[\frac{\mathrm{i}}{|x|}, -\mathrm{i}\mathcal{B}_V\right]$ has been computed above following (40). Since we are considering smooth test functions, by Taylor expansion it follows that $\phi_1(x)\phi_2(y) - \phi_1(y)\phi_2(x) = (x-y)s(x,y)$, whence $1/|y|\mathfrak{S}_1(y) = \frac{1}{|y|}G(y)$, with G smooth. Recall that our physical assumption that the electron density vanishes at the nucleus implies $G(0) = 0$. The L^2 norm of this term can be estimated using Hardy's inequality. We find that

$$\left\| \frac{1}{|y|} \mathfrak{S}_1(y) \right\|_{L^2} = \left\| \frac{1}{|y|} G(y) \right\|_{L^2} \leq \mathcal{C} = \mathcal{C}(\|\phi\|_{H^2}). \tag{55}$$

For the estimate of the H^1-norm, we compute

$$\nabla_y\left(\frac{1}{|y|}G(y)\right)=\frac{1}{|y|^2}\overrightarrow{e}_yG(y)+\frac{1}{|y|}\nabla_yG(y).$$

The L^2 norm of the second term is bounded in terms of $\|\phi\|_{H^3}$ by Hardy's inequality, while the same holds for the first term by (17). Altogether, we have shown that

$$\|\mathcal{C}_5\|_{H^1}\le\mathcal{C}(\|\phi\|_{H^3}). \tag{56}$$

Repeating the analogous derivations to compute the terms in the double commutator $[\mathrm{i}\Delta,[\mathrm{i}\Delta,-\mathrm{i}\mathcal{B}_V]]$ reveals that this contains the following terms, whose L^2-norms need to be estimated:

- From $[\mathrm{i}\Delta,\mathcal{C}_2]$,

$$\begin{aligned}\mathcal{C}_6(y) &:= \left\langle\phi_1(x)\left|\nabla_x\Delta_y\frac{1}{|x-y|}\right|\nabla_x\phi_2(x)\right\rangle_{L^2(x)}\phi_3(y) \qquad (57)\\ &= \left(\nabla_y\overline{\phi_1(y)}\cdot\nabla_y\phi_2(y)+\overline{\phi_1(y)}\Delta\phi_2(y)\right)\phi_3(y).\end{aligned}$$

It has been shown in [10] that all other terms in $[\mathrm{i}\Delta,[\mathrm{i}\Delta,-\mathrm{i}\mathcal{B}_V]]$ cancel due to antisymmetry, and that

$$\|\mathcal{C}_6\|_{L^2}\le\text{const.}\|\phi_1\|_{H^2}\|\phi_2\|_{H^2}\|\phi_3\|_{H^2}. \tag{58}$$

- Antisymmetry implies that

$$[\mathrm{i}\Delta,\mathcal{C}_3]=[\mathrm{i}\Delta,\mathcal{C}_4]=0.$$

- $[\mathrm{i}\Delta,\mathcal{C}_5]$ yields the terms

$$\mathcal{C}_7(y) := \left\langle\phi_1(x)\left|\nabla_y\frac{1}{|x-y|}\right|\phi_2(x)\right\rangle_{L^2(x)}\nabla_y\left(\frac{1}{|y|}\phi_3(y)\right), \tag{59}$$

$$\mathcal{C}_8(y) := \left\langle\phi_1(x)\left|\nabla_x\frac{1}{|x-y|}\right|\nabla_x\phi_2(x)\right\rangle_{L^2(x)}\frac{1}{|y|}\phi_3(y). \tag{60}$$

By the previous techniques, these are estimated as

$$\|\mathcal{C}_7\|_{L^2} \le \text{const.}\|\phi_1\|_{H^1}\|\phi_2\|_{H^1}\|\phi_3\|_{H^2}, \tag{61}$$

$$\|\mathcal{C}_8\|_{L^2} \le \text{const.}\|\phi_1\|_{H^1}\|\phi_2\|_{H^2}\|\phi_3\|_{H^1}. \tag{62}$$

- The commutator $[\nabla,[\mathrm{i}\Delta,-\mathrm{i}\mathcal{B}_V]]$ yields the terms

$$\mathcal{C}_9(y):=\overline{\phi_1(y)}\phi_2(y)\nabla_y\phi_3(y), \tag{63}$$

with

$$\|\mathcal{C}_9\|_{L^2}\le\mathcal{C}=\mathcal{C}(\|\phi\|_{H^2}), \tag{64}$$

minding the Hölder and Sobolev inequalities.

- Of the same origin are the terms

$$\mathcal{C}_{10}(y) := \left\langle \phi_1(x) \left| \nabla_x \nabla_y \frac{1}{|x-y|} \right| \nabla_x \phi_2(x) \right\rangle_{L^2(x)} \phi_3(y), \tag{65}$$

$$\mathcal{C}_{11}(y) := \left\langle \phi_1(x) \left| \Delta_x \frac{1}{|x-y|} \right| \nabla_x \phi_2(x) \right\rangle_{L^2(x)} \phi_3(y), \tag{66}$$

permitting estimates

$$\|\mathcal{C}_{10}\|_{L^2} \leq \text{const.} \|\phi_1\|_{H^1} \|\phi_2\|_{H^2} \|\phi_3\|_{H^1}, \tag{67}$$

$$\|\mathcal{C}_{11}\|_{L^2} \leq \text{const.} \|\phi_1\|_{H^1} \|\phi_2\|_{H^2} \|\phi_3\|_{H^1}. \tag{68}$$

- The double commutator $[\nabla, [\nabla, -\mathrm{i}\mathcal{B}_V]]$ is found to contain only contributions which, due to antisymmetry, vanish.

- $[\nabla, \mathcal{C}_5]$ yields the terms

$$\mathcal{C}_{12}(y) := \left\langle \phi_1(x) \left| \nabla_x \frac{1}{|x-y|} \right| \phi_2(x) \right\rangle_{L^2(x)} \frac{1}{|y|} \phi_3(y), \tag{69}$$

and likewise with ∇_y replacing ∇_x. Similarly as for $\mathcal{C}_1$ and $\mathcal{C}_2$, these are estimated using the Hardy and Hölder inequalities, see also (44). The estimate

$$\|\mathcal{C}_{12}\|_{L^2} \leq \text{const.} \|\phi_1\|_{H^1} \|\phi_2\|_{H^1} \|\phi_3\|_{H^1} \tag{70}$$

readily follows.

- The commutators $\left[\frac{\mathrm{i}}{|x|}, \mathcal{C}_1\right], \ldots, \left[\frac{\mathrm{i}}{|x|}, \mathcal{C}_4\right]$ imply, by the considerations following (40), multiplication of the respective terms by $\mathrm{i}/|x|$, whence by Hardy's inequality the same bounds as in (47), (48), (53) and (54) hold.

- Finally, the commutator $\mathcal{C}_{13}(y) := \left[\frac{\mathrm{i}}{|x|}, \mathcal{C}_5\right]$ is computed by multiplying $\mathfrak{S}_1(y)$ in (38) by $1/|y|^2$. Exploiting antisymmetry, we find

$$\mathcal{C}_{13}(y) = \frac{1}{|y|^2} G(y),$$

with G containing first derivatives of ϕ, cf. (55). Thus, using (17), we conclude

$$\|\mathcal{C}_{13}\|_{L^2} \leq \mathcal{C}, \quad \mathcal{C} = \mathcal{C}(\|\phi\|_{H^3}). \tag{71}$$

With the commutator bounds given above, it is clear that the proof outlined in Section 3.2 is completed analogously to [10] and Theorem 1.1 has been demonstrated.

4 Conclusions and Outlook

In this paper, we have analyzed the variational splitting integrator of [14] for the discretization in time of the MCTDHF equations of motion. The convergence in the present setting of the electronic Schrödinger equation with Coulomb interaction and singular nuclear attractive potential was investigated in Section 3.2.

We were able to establish the convergence of this time integrator. 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 [8, 14].

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