Time Dependent Closed Quantum Systems: Nonlinear Kohn-Sham Potential Operators and Weak Solutions

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Abstract

We discuss time dependent quantum systems on bounded domains from the perspective of nonlinear, time-dependent potentials. The time dependence of the Kohn-Sham potentials distinguishes this study from that of the so-called nonlinear Schrödinger equation, much studied in the mathematical community. We are interested in establishing a framework for potentials including the external potential, the Hartree potential and the exchange correlation potential as occur in time dependent density functional theory (TDDFT). As in previous work, we make use of the time-ordered evolution operator. A departure from the previous work is the use of weak solutions for the nonlinear model; this necessitates a new framework for the evolution operator based upon dual spaces. We are able to obtain unique global solutions. The author thanks Eric Polizzi for discussions leading to the incorporation of a version of the exchange correlation potential in the model.

Keywords Time dependent quantum systems, time-ordered evolution operators, Hamiltonian, Kohn-Sham potentials, unique weak solutions

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1 Introduction

This article continues the analysis of a general version of time dependent closed quantum mechanical systems, begun in [1]. The emphasis in this work was a rigorous study of discretization and well-posedness based upon the evolution operator; this is consistent with the applications' literature [2, 3, 4, 5, 6, 7]. Here, we extend the analysis to a broader class of nonlinear potentials and a broader class of solutions than considered in our previous work. In particular, we incorporate the exchange correlation potential, in addition to the Hartree potential considered in [1]. The systems which we study are confined to bounded domains with homogeneous Dirichlet boundary values. We now summarize the

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plan of the article. In the remainder of the introduction, we define the admissible nonlinear quantum systems, via the specification of the Hamiltonian operator. In the second section, we establish the framework for the evolution operator defined with respect to appropriate dual spaces. In section three, we give the details of the global existence and uniqueness theorem, achieved via the contraction mapping theorem.

1.1 Time dependent quantum systems

Classical density functional theory (DFT) transfers inter-electron effects to the exchange-correlation potential, expressed as a functional of the electron density ρ [8, 9]. This theory, and its time-dependent counterpart, TDDFT, proposed in [10], are capable of representing a many-electron system in terms of non-interacting effective particles. We allow for a realization Φ of this term below. The aggregate potential is the effective potential V_{eff}. This leads to the Hamiltonian $\hat{H}$ and its associated Kohn-Sham orbitals. For any usefulness in the applied community, the effective potential must be permitted to include a term (perhaps interpreted as an excitation term) with explicit dependence on time; in addition, the exchange correlation has a time history. This excludes the use of convolution semigroups, except as an approximation tool. The evolution operator is required.

1.2 Initial value problem for Schrödinger systems

We follow the notation and format of [11]. If we denote by $\hat{H}$ the Hamiltonian operator of the system, then the state $\Psi(t)$ of the system obeys the nonlinear Schrödinger equation,

$$i\hbar \frac{\partial \Psi(t)}{\partial t} = \hat{H}\Psi(t). \tag{1}$$

Here, $\Psi = \{\psi_1, \ldots, \psi_N\}$ and the charge density ρ is defined by [7, Eq. (2.37)]

$$\rho(\mathbf{x}, t) = |\Psi(\mathbf{x}, t)|^2 = \sum_{k=1}^{N} |\psi_k(\mathbf{x}, t)|^2.$$

For mathematical well-posedness, an initial condition,

$$\Psi(0) = \Psi_0, \tag{2}$$

consisting of N orbitals, and boundary conditions must be adjoined. We will assume in this article that the particles are confined to a bounded region $\Omega \subset \mathbb{R}^3$ and that homogeneous Dirichlet boundary conditions hold for the evolving quantum state within a closed system. In general, Ψ denotes a finite vector function of space and time. In the mathematical arguments below, we will consider the classical case of Euclidean dimension $d = 3$. In the final section, we will comment on the cases $d = 1, 2$.

1.3 Specification of the Hamiltonian operator

If, as discussed earlier, the electron charge density is defined by $\rho = |\Psi|^2$, we study potentials which are of the form,

$$V_{\text{eff}}(\mathbf{x}, t, \rho) = V(\mathbf{x}, t) + W * \rho + \Phi(\mathbf{x}, t, \rho),$$

where, for $W(\mathbf{x}) = 1/|\mathbf{x}|$, the convolution $W * \rho$ denotes the Hartree potential, and where Φ represents a time history of ρ:

$$\Phi(\mathbf{x}, t, \rho) = \Phi_0(\mathbf{x}, 0, \rho) + \int_0^t \phi(\mathbf{x}, s, \rho)\, ds.$$

As explained in [7, Sec. 6.5], Φ_0 is determined by the initial state of the Kohn-Sham system and the initial state of the interacting reference system with the same density and divergence of the charge-current.

We make the following assumptions.

- The integrand ϕ is assumed nonnegative and bounded in its arguments.
- Φ is assumed continuous in t into H^1 and bounded in t into $W^{1,3}$. The continuity into H^1 is consistent with the zero-force law as defined in [7, Eq. (6.9)]:
$$\int_\Omega \rho(\mathbf{x}, t) \nabla \Phi(\mathbf{x}, t, \rho) = 0.$$
- Furthermore, the following smoothing condition is assumed, expressed in a (uniform) Lipschitz norm condition:
$$\|\Phi(t, |\Psi_1|^2) - \Phi(t, |\Psi_2|^2)\|_{H^1} \leq C \|\Psi_1 - \Psi_2\|_{H^1},\ \forall t \in [0, T].$$
- The so-called external potential V is assumed to be continuously differentiable on the closure of the space-time domain and to be *nonnegative*.

Remark 1.1 *We do not explicitly incorporate the ionic potential.*

The Hamiltonian operator then assumes the standard form,

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V_{\text{eff}} = -\frac{\hbar^2}{2m}\nabla^2 + V(\mathbf{x}, t) + W * \rho + \Phi(t, \rho). \tag{3}$$

Although it is generally understood in the physics community that the exchange-correlation potential must include a time-history of the system, most mathematical models have avoided this, and have employed the so-called adiabatic approximation, which suppresses time history. In our inclusion of this, we have selected a term with generic properties which appear to be consistent with those derived in [12] and [7, Sec. 6.3], rather than a term represented by a formula. The type of weak solution derived in this article is now specified.

1.4 The weak solution

We require the solution to be continuous from the time interval into H_0^1. The time derivative is required to be continuous from the time interval into H^{-1}. Finally, the spatially dependent test functions are arbitrary in the space H_0^1. We formalize this.

Definition 1.1 *For $J = [0, T]$, the vector-valued function $\Psi = \Psi(\mathbf{x}, t)$ is a weak solution of (1, 2, 3) if*

$$\Psi \in C(J; H_0^1(\Omega)) \cap C^1(J; H^{-1}(\Omega)),$$

if Ψ satisfies the initial condition (2) for $\Psi_0 \in H_0^1$, and if $\forall\, t \in J$ the following integral relation holds for $\rho = |\Psi|^2$:

$$i\hbar\langle \frac{\partial \Psi(\mathbf{x}, t)}{\partial t}, \bar{\zeta}(\mathbf{x})\rangle = \int_\Omega \left\{ \frac{\hbar^2}{2m} \nabla\Psi(\mathbf{x}, t) \cdot \nabla\bar{\zeta}(\mathbf{x}) + V_{\text{eff}}(\mathbf{x}, t, \rho)\Psi(\mathbf{x}, t)\bar{\zeta}(\mathbf{x}) \right\} d\mathbf{x}.$$

Here, $\zeta \in H_0^1(\Omega)$ is arbitrary and V_{eff} is a function of ρ.

The analytical part of this article will establish the existence of a unique global weak solution via the evolution operators. This solution is valid for the vector-valued function Ψ as defined. The function spaces correspondingly contain N function components. The hypothesis on the time history may appear stringent. However, the full strength of the hypothesis is required to verify the similarity hypothesis on the Hamiltonian (cf. Proposition 2.2); this is needed to establish invariance of the evolution operators on H_0^1. The theory as developed here considers a natural pairing (H^{-1}, H_0^1) connected by isomorphism. The evolution operators are constructed on H^{-1} and are shown to be stable on H_0^1. At the conclusion of the article, we raise as a question for further study whether already demonstrated pairings, specifically the (L^2, H^2) pairing discussed in [1], can imply the (H^{-1}, H_0^1) pairing.

2 The Evolution Operator on Dual Spaces

We employ here the theory originally derived by Kato and Dorroh [13, 14, 15] and described in [16]. The theory requires stable C_0-semigroup generation on a frame space X, leading to time interval norm operator continuity from a smooth space Y to X and semigroup invariance on the smooth space. There is an alternative approach discussed in [17, Theorems X.70, X.71], based on the derivative of certain residual quantities, which is not employed here.

2.1 Semigroup generation on the dual space

In order to obtain a semigroup generation result which is contractive for all time t, we treat H^{-1} as a reflexive Banach space, as discussed in [18]. This will serve as the frame space X on which the evolution operators will be derived.

The reader will recall that the natural tool in the case of Hilbert space for semigroup generation via skew-adjoint generators is the theorem of Stone on unitary group generation. We will need a replacement of this theorem which yields contractive semigroups on the reflexive Banach space H^{-1} via the family of generators $(-i/\hbar)\hat{H}$. This is the Lumer-Phillips theorem. We quote a version of it here (cf. [19], [20, Cor. 3.20, p. 86]) applicable to reflexive Banach spaces.

Theorem 2.1 *(Lumer-Phillips: reflexive Banach spaces) If Z is a reflexive Banach space, and $G : D(G) \subset Z \mapsto Z$ is a linear operator, then G is the generator of a contraction semigroup if and only if the following two conditions hold:*

- *G is dissipative.*
- *$G - \lambda_0 I$ is surjective for some $\lambda_0 > 0$.*

For readers unfamiliar with these terms, we give brief definitions. For the dissipative property, it is convenient to use the characterization given in [20, Prop. 3.23].

Definition 2.1 *A C_0-semigroup $\{T(t)\}$ is contractive on a Banach space Z if $\|T(t)\| \leq 1$ for all $t \in [0, T]$. The operator G is dissipative if*

$$\text{Re } \langle Gf, j(f)\rangle \leq 0,$$

for all $f \in D(G)$, where $j(f)$ is an element in the duality set for f. If Z is reflexive, this is the unique element $j(f) = \psi \in Z^*$ satisfying

$$\psi(f) = \langle f, \psi\rangle = \|f\|^2 = \|\psi\|^2.$$

Definition 2.2 *Suppose the Hamiltonian is represented as previously, with $\rho = |u|^2$ and $u \in C(J, H_0^1)$. We define the family $A(t) = \frac{i}{\hbar}\hat{H}(t, \rho)$ to be the operators with domain $D(A) \subset H^{-1}$ independent of t as follows.*

$$\begin{aligned} D(A) &= H_0^1, \\ (A(t)f)(w) &= (i/\hbar)\int_\Omega [V_{\text{eff}}(\cdot\,, t, \rho)fw + \frac{\hbar^2}{2m}\nabla f\cdot\nabla w]\, d\mathbf{x}. \end{aligned} \tag{4}$$

Proposition 2.1 *The family $A(t)$ satisfies the conditions of the Lumer-Phillips theorem, with the identification: $G = -A(t)$. It follows that $-A(t)$ generates a family of contraction semigroups on H^{-1}. The family is also stable on H^{-1}. This means:*

$$\|\prod_{j=1}^{k}[A(t_j) + \lambda]^{-1}\| \leq \lambda^{-k}, \ \ \textit{for } \lambda > 0, \tag{5}$$

for any finite family $\{t_j\}_{j=1}^k$, with $0 \leq t_1 \leq \cdots \leq t_k \leq T$. Moreover, $\prod$ is time-ordered: $[A(t_\ell) + \lambda]^{-1}$ is to the left of $[A(t_j) + \lambda]^{-1}$ if $\ell > j$.

Proof: We begin by observing that $A(t)$ is well-defined. This means that the range of $A(t)$ is in H^{-1} for each t. This is clear, since the term V_{eff} is actually bounded on the space-time domain. We now establish the dissipative property. By use of the bidual mapping to represent the second dual of H_0^1, we may conveniently define $j(f) \in H^{-1^*} = H_0^1$ via complex conjugation of f: $j(f) = \bar{f}$. This definition, coupled with the fact that V_{eff} is real-valued, implies that

$$\text{Re } \langle A(t)f, j(f)\rangle = 0.$$

We claim that the range of $A(t) + \lambda I$ is, in fact, equal to H^{-1} for all positive λ. We observe that the Hamiltonian is closed; in fact, the operator $\frac{-1}{h^2}\nabla^2$ is self-adjoint and hence closed [21] when H^{-1} is given the equivalent topology of a real Hilbert space, since the property of being closed is preserved under the equivalent topology of H^{-1}. Moreover, the operator defined by the potential multiplier is uniformly bounded on a dense set of continuous linear functionals, those that are defined by L^2 functions [18], so that the Hamiltonian, and hence the operator $A(t)$, is closed. Thus, it suffices to show that the range of $A(t)+\lambda I$ is dense in H^{-1}. Suppose this is *not* the case for a specific λ; there is a *nonzero* continuous linear functional on H^{-1} which has a zero evaluation on the range. This is a consequence of the Hahn-Banach theorem [22]. We demonstrate now that any continuous linear functional on H^{-1}, which vanishes on the range of $A(t) + \lambda I$, must be zero. We again make use of the bidual mapping. Consider $v \in H_0^1$ such that

$$\langle A(t)f + \lambda f, v\rangle = 0,$$

for all $f \in D(A(t))$. By selecting f to be the complex conjugate of v, and subsequently taking the real part, one has

$$\lambda \int_\Omega |v|^2 \, d\mathbf{x} = 0,$$

which implies that $v = 0$. One concludes that the range is dense for all positive λ. This establishes the existence of contractive semigroups by the Lumer-Phillips theorem. The stability follows from the equivalence of resolvent estimates with the contractive property. □

Remark 2.1 *Before proceeding to the similarity transformation which permits the conclusion that the semigroup is invariant on $D(A)$, we comment on the real Hilbert space approach outlined in [21] for isometric groups. One can carry this out by using a Hilbert space norm on H^{-1} which is dependent on a specific $A(t)$. We have preferred the standard dual space characterization, because of the nature of our approach to the time-dependent Hamiltonian.*

2.2 Characterization of the smooth space H_0^1 and the isomorphism S

We define H_0^1 to coincide with $D(A)$ as defined in (4). In addition, the standard (complex) inner product and norm are adopted on $H_0^1 \subset H^1$. There is a well-known isomorphism which relates H^{-1} and H_0^1 considered as distinct Banach

spaces. This isomorphism plays an essential role in the theory of the evolution operators. In order to conform to the traditional notation, we define S as follows: given $v \in H_0^1$ and $\zeta \in H_0^1$, define $f = S(v)$ as the continuous linear functional

$$f(\zeta) = \int_\Omega \left[v\zeta + \frac{\hbar^2}{2m} \nabla v \cdot \nabla \zeta \right] \, d\mathbf{x}.$$

Standard methods show that S is an isomorphism.

2.3 Continuity of $A(t)$ into $B[H_0^1, H^{-1}]$ and semigroup invariance on H_0^1

We are in the process of verifying the conditions which are sufficient for the existence of the evolution operator. These are listed in detail in [16, Ch. 6] or in summary form in the appendix of [1]. Once again, we suppose that $u \in C(J; H_0^1)$, and $\rho = |u|^2$, which defines the Hamiltonian. We make the preliminary observation that $A(t) : J \mapsto B[H_0^1, H^{-1}]$ is continuous in t. It is routine, based upon our earlier arguments, to show that $A(t)$ is well-defined in $B[H_0^1, H^{-1}]$. Continuity involves an analysis of terms of the form, for fixed $\rho(t)$:

$$\int_\Omega [V_{\text{eff}}(\cdot\,, t, \rho) - V_{\text{eff}}(\cdot\,, s, \rho)] v\zeta d\mathbf{x}, \tag{6}$$

where $\zeta \in H_0^1$ is a 'test function' and v is the operator target of the potential. The hypotheses allow the application of the Hölder inequality to each component term of (3). We summarize. For the external potential, one has continuity from the time interval into the space of bounded measurable functions; this is implied by the regularity assumed for V. For the Hartree potential, one has, by Young's inequality,

$$\begin{aligned} &\text{For } t, s \in J, \ \|W * (|u(\cdot\,, t)|^2 - |u(\cdot\,, s)|^2)\|_{L^{3/2}} \\ &\leq \|W\|_{L^{3/2}} \||u(\cdot\,, t)|^2 - |u(\cdot\,, s)|^2\|_{L^1}. \end{aligned}$$

Factorization of the difference of squares, together with Sobolev's inequality, now yields continuity in t in the $L^{3/2}$ norm, permitting the application of the Hölder inequality to this term as represented in (6). The assumptions made on Φ directly ensure that Φ defines a continuous mapping into $B[H_0^1, H^{-1}]$.

We now discuss the property of semigroup invariance on the smooth space.

Proposition 2.2 *The semigroups of Proposition 2.1 remain stable on H_0^1. In particular, the evolution operator $U(t, s)$ exists for this case for fixed ρ. Moreover, (10) to follow holds rigorously.*

Proof: We are using the theory of Kato as presented in [16], and we make use of S and S^{-1} introduced above. It will be useful in the proof to make the observation that

$$\hat{H}(t) = S - I + V_{\text{eff}}.$$

The proof entails the verification of the similarity relation,

$$SA(t)S^{-1} = A(t) + B(t),$$

for a family $B(t)$, which can be extended as bounded linear operators on H^{-1}. As previously, $A(t) = \frac{i}{\hbar}\hat{H}(t)$. The domain of the operator $A_1(t) = SA(t)S^{-1}$ is H_0^1. Specifically, as noted in [16, Prop. 6.2.4],

$$D(A_1) = \{f \in H^{-1} : S^{-1}f \in H_0^1, AS^{-1}f \in H_0^1\},$$

which here is H_0^1. We make a reduction prior to the analysis. It is equivalent to verify that

$$S\hat{H}(t)S^{-1} = \hat{H}(t) + B(t),$$

where $B(t)$ represents a bounded operator on (all of) H^{-1}. This relation retains its structure under multiplication by i. The bound obtained will hold uniformly in $t \in [0, T]$. By use of the definitions we explicitly obtain the representation for $B(t)$. Note that

$$B(t) = S\hat{H}(t)S^{-1} - \hat{H}(t) = [S, \hat{H}(t)]S^{-1},$$

where $[S, \hat{H}(t)]$ is the commutator of S and $\hat{H}$. By taking cancellation into consideration, and writing $u = S^{-1}\ell$, we have, for the extension of $B(t)$ from the domain H_0^1 of $A(t)$ to H^{-1}:

$$\langle B(t)\ell, \zeta\rangle = \int_\Omega \left[\frac{\hbar^2}{2m} u\nabla V_{\text{eff}} \cdot \nabla\zeta\right] \, d\mathbf{x}, \ \forall \zeta \in H_0^1. \tag{7}$$

The estimation of the external potential is immediate from the hypotheses. The derivative of Φ can be estimated by the hypotheses: boundedness from the time interval into $W^{1,3}$ allows one to apply the Hölder and Sobolev inequalities with an L^3 gradient for the potential term. This bound is uniform in t. In particular, it is really the derivative of the Hartree potential which requires close examination. We claim that it is an L^3 function in x, with a norm bound independent of t. This is sufficient to show that this term defines a bounded linear operator, with bound uniform in t, as required. Thus, we differentiate the convolution, to obtain $W_{x_i} * \rho$. The standard rules for differentiating W yield that W_{x_i} has a singularity near the origin of order $1/|x|^2$. The application of spherical coordinate integration on a bounded domain yields that this is an L^1 function; by Hölder's inequality, we conclude that the differentiated convolution inherits the L^3 property of ρ. Finally, there is a measure theory requirement, which is satisfied for the current application, for the perturbation $B(t)$, as discussed in [16, Prop. 7.1.4] and the discussion preceding it. Because of the technical nature of the requirement, we simply cite the reference, where complete details are given. In particular, the representation (10) holds rigorously. This completes the proof. □

We have cataloged the properties of the evolution operator in [1]. They can be found in the reference [16].

2.4 The general initial value problem

The evolution operator permits the solution of the linear Cauchy problem,

$$\frac{du}{dt} + A(t)u(t) = F(t), \tag{8}$$

$$u(0) = u_0, \tag{9}$$

on an interval $[0,T]$, with values in the Banach space H^{-1}. The solution is given by

$$u(t) = U(t,0)u_0 + \int_0^t U(t,s)\ F(s)\ ds, \tag{10}$$

under assumptions on u_0, F. In what follows, we apply this to the case $F = 0$ and $u_0 \in H_0^1$. The interpretation of (10) is that of the existence of a weak solution $u(t) \in H_0^1,\ \forall t \in J$.

3 Unique Global Weak Solution

We begin with the definition of a key mapping.

Definition 3.1 *For $J = [0,T], T$ arbitrary, define $K : C(J; H_0^1) \mapsto C(J; H_0^1)$:*

$$Ku(\cdot\,, t) = U^u(t,0)\Psi_0.$$

$U = U^u$ has been defined and established in Proposition 2.2, where $\rho = |u|^2$.

Remark 3.1 *We will require estimates of $\|U^u(t,s)\|_{H^{-1}}$ and $\|U^u(t,s)\|_{H_0^1}$. The use of contraction semigroups implies that on H^{-1} the evolution operators are bounded by one in norm. On H_0^1, the operators $U^u(t,s)$ have norm which is bounded from above by a constant C with dependency, $C(T, \|u\|_{C(J;H_0^1)})$ (see [16, Cor. 6.3.6]). A bound for $\|u\|$ in $C(J; H_0^1)$ is given by Lemma 3.1 to follow.*

Theorem 3.1 *There is a closed ball $\overline{B(0,r)} \subset C(J, H_0^1)$ on which K is invariant. For t sufficiently small, K defines a strict contraction. The contraction constant is independent of the restricted time interval, so that the unique fixed point can be continued globally in time. In particular, for any interval $[0,T]$, the system has a unique solution which coincides with this fixed point.*

Proof: We use Lemma 3.1 to follow, based on a conservation principle, to obtain the invariant closed ball $\overline{B(0,r)}$. By the construction, this ball is invariant over $[0,T]$. In order to estimate the Lipschitz constant of K, the following identity is pivotal [16, Eq. (7.1.3)]:

$$U^{\hat{u}}\Psi_0(t) - U^{\hat{v}}\Psi_0(t) = -\int_0^t U^{\hat{u}}(t,s)[A^{\hat{u}}(s) - A^{\hat{v}}(s)]U^{\hat{v}}(s,0)\Psi_0\ ds. \tag{11}$$

The H_0^1-norm of the evolution operators can be bounded by a constant which depends only on the terminal time T and the bound discussed in Lemma 3.1. Thus, the essential term is:

$$\|V_{\rm eff}(|\hat{u}|^2) - V_{\rm eff}(|\hat{v}|^2)\|_{C(J;H_0^1)}.$$

The estimate for the external potential and the correlation potential have been built into the hypotheses. The estimate for the Hartree potential has already been carried out above in the proof of Proposition 2.2. The time integral representation in (11) for the mapping yields the result for t sufficiently small. The continuation is possible because the Lipschitz constant depends only upon T. □

We now discuss the conservation principle for this system. In fact, we will establish the following:

- If the conservation functional $\mathcal{E}$ is defined for $0 < t \leq T$ by,

$$\mathcal{E}(t) = \int_\Omega \left[\frac{\hbar^2}{4m} |\nabla \Psi|^2 + \left(\frac{1}{4}(W * |\Psi|^2) + \frac{1}{2}(V + \Phi) \right) |\Psi|^2 \right] \, dx_1 dx_2 dx_3,$$

  then the following identity holds:

$$\mathcal{E}(t) = \mathcal{E}(0) + \frac{1}{2} \int_0^t \int_\Omega [(\partial V/\partial r)(\mathbf{x}, r) + \phi(\mathbf{x}, r, \rho)] |\Psi|^2 \, dx_1 dx_2 dx_3 dr, \qquad (12)$$

where $\rho = |\Psi|^2$, and

$$\mathcal{E}(0) = \int_\Omega \left[\frac{\hbar^2}{4m} |\nabla \Psi_0|^2 + \left(\frac{1}{4}(W * |\Psi_0|^2) + \frac{1}{2}(V + \Phi_0) \right) |\Psi_0|^2 \right] \, dx_1 dx_2 dx_3.$$

The functional $\mathcal{E}(t)$ is related to the physical energy $E(t)$ of the system, defined by

$$E(t) = \langle \hat{H}(t)\Psi(t), \Psi(t) \rangle,$$

as follows:

$$\mathcal{E}(t) = \frac{1}{2} \left(E(t) - \frac{1}{2} \langle \Psi(t), (W * |\Psi(t)|^2)\Psi(t) \rangle \right).$$

We first observe that (12) is sufficient to imply that the functions $\{\Psi\}$ are bounded in $C(J; H_0^1)$; indeed, L^2 gradient bounds for Ψ are obtained from $\mathcal{E}(t)$. These bounds depend only on Ψ_0, V, Φ, and the time derivative of V. Note that Ψ has H^{-1} norm less than or equal to that of Ψ_0. Also, solutions of this system have invariant L^2 norms (see [23] for the standard argument).

Lemma 3.1 *The value of $\mathcal{E}$ at any time t is given by (12). In fact, this implies that the $C(J; H_0^1)$ norm has an invariant bound for any solution of the system.*

Proof: It remains to verify (12); in fact, we establish its derivative:

$$0 = \frac{d\mathcal{E}}{dt} - \frac{1}{2} \int_\Omega [(\partial V/\partial t)(\mathbf{x}, t) + \phi(\mathbf{x}, t, \rho)] |\Psi|^2 \, dx_1 dx_2 dx_3. \qquad (13)$$

We use the system as described in Definition 1.1 together with the relation between $\mathcal{E}(t)$ and $E(t)$ above in order to prove the following relation, which is equivalent to (13):

$$\begin{aligned}\frac{d\mathcal{E}}{dt} &= \underbrace{\mathrm{Re}\,\langle \hat{H}(t)\Psi(t), (\partial\Psi(t)/\partial t)\rangle}_{=0} + \frac{1}{2}\langle (\partial\hat{H}(t)/\partial t)\Psi(t), \Psi(t)\rangle \\ &- \frac{1}{4}(\partial/\partial t)\langle \Psi(t), (W * |\Psi(t)|^2)\Psi(t)\rangle.\end{aligned}$$

This makes transparent the cancellation of the Hartree term. However, an immediate difficulty is that $\partial\bar{\Psi}/\partial t$ is in H^{-1}. We require a substitute for the following formal operation: multiply the system by $\partial\bar{\Psi}/\partial t$, integrate over Ω, and take the (vanishing) real part. This is a standard technique and yields (13) formally. For the general result, we use the extrapolation method for the Laplacian, as described in [21, Ch. 2]; this method extends this self-adjoint operator domain to H^{-1}. The remaining part of the Hamiltonian range is designed to be in H_0^1, so that the application of $\partial\bar{\Psi}/\partial t$ is justified. We may thus conclude that dual operations, formally equivalent to the operations on functions just described, lead to (13). This concludes the proof. □

Remark 3.2 *As demonstrated in [1], the discretization of the evolution operator provides an effective numerical procedure for solving the the time dependent density functional system. This depends, of course, upon the algorithms introduced in [11].*

4 Summary and Future Work

4.1 Summary

Time dependent density functional theory with Kohn-Sham potentials has emerged as a significant modeling tool at quantum scales. This is substantiated by the references in this article. TDDFT is to be distinguished from the nonlinear Schrödinger equation, much studied in the mathematical community, by the presence of explicit time dependent potentials. The latter would appear to require the evolution operator rather than convolution semigroups. In this article, as well as the previous one [1], we have relied on the theory introduced by Kato in the 1970s in order to accomplish this. In the current article, we establish, via the linear theory and a continuation based on the contraction mapping principle, the existence of a unique weak solution of the TDDFT closed system on a bounded domain with homogeneous Dirichlet boundary conditions. It is well fitted to applications such as energy profiles of occupied orbitals in Carbon nanotubes [1]. Although the ground space for the evolution operator is typically L^2, as in [1], it is H^{-1} in the present work. This has required additional theory not needed in earlier construction of the evolution operator. We will comment further on this point in the following section. We have not employed

explicit formulas for the exchange-correlation potential term, but have used instead an operational definition, consistent with the literature [7], including a mildly smoothing hypothesis. In addition, we have bypassed the so-called local adiabatic assumption, which is somewhat controversial. The analysis has been assisted by a conservation principle based upon a weighted difference between the usual energy and the Hartree component.

An interesting question is whether the contraction mapping principle used in this article for the existence of a unique fixed point carries over to the earlier article [1], which employs the Leray-Schauder theorem for existence, and does not establish uniqueness. The answer is negative, even for the case considered there, where the exchange-correlation potential is not included. Indeed, one would define the (contraction) fixed point mapping on $C([0,T];H^2(\Omega)\cap H_0^1(\Omega))$, in order to use (11); however, the conservation principle is not adequate to define the closed ball on which the contraction mapping principle can be applied. On the other hand, one can obtain uniqueness from the results of this article, since a weak solution is a classical solution if one has the linear evolution theory for the pair $(L^2, H^2 \cap H_0^1)$.

4.2 Perspectives for future work

Directions for future work include: (1) explicit inclusion of the ionic potential; (2) a relaxing of the positivity of the external potential; (3) extension of the theory to non-closed systems; (4) less stringent regularity of the exchange-correlation term.

In addition to these, we cite two additional problem areas.

- The first relates to the system in Euclidean dimensions $d = 1, 2$, where the singularity of the Hartree potential presents special consideration. We suggest a shielding of the singularity by so-called soft Coulomb potentials [24, above Eq. (16)]. We believe that the theory will cover this case. In one dimension, the unshielded singularity very likely requires the Hilbert transform, and a separate study.

- If the evolution operators have been verified for the $(L^2, H^2 \cap H_0^1)$ isomorphism pairing, is there an extrapolation method which extends the family to the (H^{-1}, H_0^1) pairing? If such a result were true, then part or all of the second section could possibly be eliminated. We used a specialized form of this result in the proof of the conservation principle by using the result of [21] on the extrapolation of m-dissipative operators, which allows there the concomitant extrapolation of convolution semigroups. We propose this as a question for future study.

A Comments

The smoothing condition on Φ stated at the bottom of page three can be weakened. The weakened version is:

$$\|[\Phi(t,|\Psi_1|^2)-\Phi(t,|\Psi_2|^2)]\psi\|_{H^1} \leq C\|\Psi_1-\Psi_2\|_{H^1}\|\psi\|_{H_0^1},\ \forall t\in[0,T].$$

Here, ψ is arbitrary in H_0^1. A parallel inequality is satisfied by the Hartree potential.

For simplicity, we have assumed that the leading part, $\Phi(\cdot\,,0,\rho)$, is conserved, up to a positive constant multiple. This holds for convolutions and other important examples.

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