On the time-dependent Hartree-Fock equations coupled with a classical nuclear dynamics *

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Abstract

We prove a global-in-time existence and uniqueness result for the Cauchy problem in the setting of some model of Quantum Molecular Chemistry. The model we are concerned with consists of a coupling between the time-dependent Hartree-Fock equations (for the electrons) and the classical Newtonian dynamics (for the nuclei). The proof combines semigroup techniques and the Schauder fixed-point theorem. We also extend our result in order to treat the case of a molecule subjected to a time-dependent electric field.

Résumé

Nous montrons que le problème de Cauchy global pour un modèle de Chimie Quantique moléculaire est bien posé. Le système que nous étudions couple d'une part les équations de Hartree-Fock dépendantes du temps qui décrivent l'évolution de la configuration électronique de la molécule, et d'autre part les équations de la dynamique Newtonienne qui régissent le mouvement des noyaux. On utilise les techniques de semi-groupes pour traiter l'évolution et un argument de point fixe pour traiter le couplage. Le même problème est ensuite étudié en présence d'un champ électrique dépendant du temps.

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1 Introduction

Most of the calculations performed in Quantum Chemistry at present are devoted to solving (an approximation of) the *time-independent* Schrödinger equation. Many interesting extremely accurate results can be obtained in this manner such as the calculation of the ground state of a molecule containing several hundreds of electrons along with its electronic or vibrational spectrum.

However, such an approach is most often inadequate to study dynamical phenomena such as chemical reactions and it is then necessary to resort to the *time-dependent* Schrödinger equation. As in the stationary setting, directly tackling the numerical solving of the Schrödinger equation for computing a chemical system, even a small system like a water molecule, remains out of the scope of the computers available at present and most probably in the near future. Consequently, efficient approximations are needed. Our purpose in this article is to investigate the well-posedness of the Cauchy problem associated with one of these approximations, namely a time-dependent electronic Hartree-Fock dynamics coupled with a classical nuclear dynamics of Hellman-Feynman type. In our opinion, this model, or similar models which share the same mathematical features, are about to play an important role in Quantum Chemistry calculations.

Having briefly recalled some general mathematical properties of the Cauchy problem associated with the time-dependent Schrödinger equation in a general setting we present in Section 2 a few techniques used to approximate this equation in the specific framework of Quantum Chemisty. In particular, we introduce and compare the adiabatic and the non-adiabatic approximations which both allow one to treat separately the motion of the nuclei and that of the electrons. We also present the time-dependent Hartree-Fock approximation which permits one to deal with the electronic motion in the non-adiabatic approximation.

In Section 3, we consider (for the sake of simplicity) a Helium atom (consisting of one nucleus and two electrons), and we write up for this system the Cauchy problem associated with a non-adiabatic approximation of the Schrödinger equation in which the electrons obey the time-dependent Restricted Hartree-Fock equations and in which the nuclear-electron interaction is of Hellman-Feynman type. The system we are concerned with is thus the following:

$$\left\{ \begin{array}{l} i\dfrac{\partial \phi}{\partial t}(t,x) = -\Delta\phi(t,x) + V(x-\bar{x}(t))\phi(t,x) + \left(|\phi|^2 \star \dfrac{1}{|x|}\right)(t,x)\phi(t,x) \\ m\dfrac{d^2\bar{x}}{dt^2}(t) = \langle \phi(t)|\nabla V(\cdot - \bar{x}(t))|\phi(t)\rangle \\ \phi(0,\cdot) = \phi^0, \quad \bar{x}(0) = \bar{x}^0, \quad \dfrac{d\bar{x}}{dt}(0) = \bar{v}^0, \end{array} \right.$$

where $V(x) = -\frac{2}{|x|}$. Our main result is the proof of the well-posedness of this Cauchy problem, i.e. the global existence and uniqueness of the solution $(\phi, \bar{x})$ in the class

$$X = (C^1([0,+\infty[, L^2(\mathbb{R}^3)) \cap C^0([0,+\infty[, H^2(\mathbb{R}^3))) \times C^2([0,+\infty[, \mathbb{R}^3),$$

provided $\phi^0 \in H^2(\mathbb{R}^3)$. We have based our proof on semigroup techniques which are perfectly adapted when looking for strong solutions. We have not found it necessary to try to weaken the regularity of the initial electronic state because the assumption $\phi^0 \in H^2(\mathbb{R}^3)$ does not seem restrictive to us from a physical point of view (let us recall that, in particular, stationary electronic Hartree-Fock states have such a regularity). The local existence (Section 3.2) is established by the Schauder fixed point theorem, using in particular some properties of the propagator for the family of linear Hamiltonians $-\Delta + V(\cdot - \bar{x}(t))$ proved in a paper by Yajima [22]. The uniqueness (Section 3.3), which is obtained by the Gronwall Lemma, is based on estimates for the norm of the electronic wave function in the Lorentz space $L^{3,\infty}$. Finally, the global existence follows from the charge and energy conservations. We have chosen here not to present the simplest proof, but one which treats the three fundamental difficulties, namely the non-local nonlinearity $(|\phi|^2 \star \frac{1}{|x|})\phi$, the Coulomb singularity carried by the nuclear motion and the nonlinear coupling between the electronic and nuclear dynamics, with general techniques. Consequently, it is important to note that our proof and our principal result can both be extended to any molecular system containing a finite number of electrons and nuclei modelled by the electronic Hartree-Fock equations coupled with a classical Hellman-Feynman type nuclear dynamics.

In Section 4, we extend the global existence and uniqueness result established in Section 3 to the case when the molecular system under study is subjected to a time-dependent uniform electric field. The results obtained in the final section can be seen as a step towards the mathematical understanding of an evolving domain in Chemistry: the optimal laser control of chemical reactions. This technique has just emerged a few years ago. It consists in controlling the behavior of chemical systems (described by the Schrödinger equation), the control parameter being the electric field generated by lasers. Technical capabilities available at the present time allow one to produce ultrafast modulations of the amplitude and phase of laser pulses so that efficient control can be achieved. This is confirmed by various theoretical studies. Moreover, experimental evidence of laser control of simple chemical reactions has been published. We refer the reader to [4] and [20] and to the references therein. The numerical search for optimal control is only conceivable for *approximations* of the Schrödinger equation such as that studied in this article. The result we obtain in Section 4 ensures the well-posedness of the evolution equation for a large class of control parameters. Therefore, we are preparing some ground work in order to tackle the control issues in future studies.

2 Approximations of the time-dependent Schrödinger equation for molecular systems

The time-dependent Schrödinger equation in its general form reads

$$i\frac{\partial \psi}{\partial t} = H(t)\,\psi,$$

where for any t, the Hamiltonian $H(t)$ is a self-adjoint linear operator acting on the Hilbert space of the physical states, here denoted by $\mathcal{H}$, and the wave function $\psi(t)$ is an element of $\mathcal{H}$ of norm one. This equation completely describes the evolution of the quantum system under consideration.

2.1 General setting

Let us begin this Section with a brief overview of some mathematical results known to this day on the time-dependent Schrödinger equation in this general setting. If the system is isolated, the Hamiltonian $H(t)$ is independent on the variable t. In this case, the well-posedness of the Cauchy problem

$$\begin{cases} i\dfrac{\partial \psi}{\partial t} = H\,\psi, \\ \psi(0) = \psi^0, \end{cases}$$

with $\psi^0 \in \mathcal{H}$ is guaranteed by the Stone's theorem. More precisely, the evolution of the system is governed by a group of unitary operators on $\mathcal{H}$, the so-called propagator $(U(t,s))_{(t,s)\in\mathbb{R}^2}$, which satisfies

$$\psi(t) = U(t,s)\psi(s), \quad \text{for all } (t,s) \in \mathbb{R}^2,$$

and enjoys the following properties:

1. $U(t,s)\,U(s,r) = U(t,r)$ for all $(t,s,r) \in \mathbb{R}^3$;
2. $U(t,s)$ is unitary on $\mathcal{H}$ for all $(t,s) \in \mathbb{R}^2$ and $(t,s) \mapsto U(t,s)$ is strongly continuous from $\mathbb{R}^2$ to $\mathcal{L}(\mathcal{H})$;
3. denoting by D the domain of the operator H, $U(t,s) \in \mathcal{L}(D)$ for all $(t,s) \in \mathbb{R}^2$ and $(t,s) \mapsto U(t,s)$ is strongly continuous from $\mathbb{R}^2$ to $\mathcal{L}(D)$;
4. the equalities $i\frac{dU(t,s)}{dt} = H\,U(t,s)$ and $i\frac{dU(t,s)}{ds} = -U(t,s)\,H$ hold strongly as equalities between operators from D to $\mathcal{H}$.

From now on, we denote by $\mathcal{L}(E)$ the vector space of bounded linear maps from a normed vector space E onto itself. In view of the time-invariance, we have in addition in this case $U(t,s) = U(t-s) = e^{-i(t-s)H}$.

On the other hand, when the Hamiltonian explicitly depends on t, which happens in particular when an external time-dependent electric field is turned on, the existence of a propagator may be difficult to establish. A few general results exist, in particular the Kato's theorem [12], but they cannot be used in all cases. For instance, for $\mathcal{H} = L^2(\mathbb{R}^3)$ and $H(t) = -\Delta + V + \mathcal{E}(t)\cdot x$ with $V(x) = -\frac{Z}{|x|}$ (a particle in a fixed Coulomb potential subjected to a time-dependent electric field $\mathcal{E}(t)$) the Kato's theorem permits to conclude *provided* the time-dependent part of the potential is regular enough, which in the above setting means $t \mapsto \mathcal{E}(t)$ is continuous [11]. On the contrary, it is not sufficient to conclude for $\mathcal{H} = L^2(\mathbb{R}^3)$ and $H(t) = -\Delta + V + W(t)$ with $V(x) = -\frac{Z}{|x|}$ and $W(t,x) = \frac{1}{|x-\bar{x}(t)|}$ (which for instance models a particle placed in a fixed attractive Coulomb potential V and interacting with a moving charged particle through the interaction potential W) because of the singularity of the time-dependent potential. In this latter situation, which occurs for example in the study of collision processes, the existence of the propagator may be established either as in [21] by locally deforming the set of coordinates so that the moving particle (thus the singularity) remains fixed in this frame (let us note that such an approach allows one to conclude only when the time-dependent part of the potential is of the general form $W(t,x) = W(x - \bar{x}(t)))$, or as in [22] by resorting to $L^p - L^q$ estimates provided the time-dependent part of the potential is not too singular (the Coulomb singularity being convenient in $\mathbb{R}^3$).

Let us now turn to the specific framework of Quantum Chemistry. We consider a chemical system consisting of M nuclei and of N electrons. Denoting by m_k the mass of the k-th nucleus and z_k its charge, the "exact" non-relativistic Hamiltonian reads

$$\begin{aligned} H &= -\sum_{k=1}^{M} \frac{1}{2\,m_k} \Delta_{\bar{x}_k} - \sum_{i=1}^{N} \frac{1}{2} \Delta_{x_i} - \sum_{i=1}^{N} \sum_{k=1}^{M} \frac{z_k}{|x_i - \bar{x}_k|} \\ &\quad + \sum_{1 \le i < j \le N} \frac{1}{|x_i - x_j|} + \sum_{1 \le k < l \le M} \frac{z_k\, z_l}{|\bar{x}_k - \bar{x}_l|}. \end{aligned} \tag{1}$$

The first term in the Hamiltonian H represents the kinetic energy of the nuclei, the second term that of the electrons, the third term the attraction between electrons and nuclei, the fourth and the fifth terms the interelectronic and the internuclear repulsions respectively. The units used for writing this Hamiltonian are the so-called atomic units, which are the most wide-spread in Quantum Chemistry: in this unit system, the Planck constant $\hbar$, the mass of the electron, the elementary charge and the factor $\frac{1}{4\pi\epsilon_0}$ are all set to one (ϵ_0 denotes the dielectric constant of the vacuum). The space of the physical states reads

$$\mathcal{H} = \mathcal{H}_n \otimes \mathcal{H}_e, \quad \text{with } \mathcal{H}_e = \bigwedge_{i=1}^{N} L^2(\mathbb{R}^3, \mathbb{C}^2), \quad \mathcal{H}_{\mathrm{n}} \subset \bigotimes_{\mathrm{k}=1}^{\mathrm{M}} \mathrm{L}^2(\mathbb{R}^3, \mathbb{C}^{2\mathrm{s}_\mathrm{k}+1}),$$

where $\mathcal{H}_n$ and $\mathcal{H}_e$ denote respectively the subspaces of the nuclear and electronic wave functions and s_k the spin of the k-th nucleus. The expression of $\mathcal{H}_n$ depends on the nature of the nuclei. In particular, it takes into account the indicernibility or more precisely the fermionic or bosonic nature of nuclei of same nature (same number of protons and of neutrons). From a purely theoretical point of view, the "exact" Cauchy problem for such a chemical system is well-posed from the Stone's theorem because of the self-adjointness of the Hamiltonian (*see* [17]). However, for chemical systems made up of more than two or three particles, this problem is of too much a large size to be directly tackled by standard numerical methods and it is then necessary to approximate it.

2.2 The adiabatic approximation

A standard approximation method is the so-called adiabatic approximation. Briefly speaking, it consists in getting rid of the fast dynamics of the electrons by assuming that at any time the electrons are in the electronic ground state, which of course depends on the time *via* the nuclear coordinates (for the sake of completeness, let us however mention that in a few studies the adiabatic approximation means that the electrons remain in the k-th excited state, k being independent of time; we shall only deal here with the ground state). More precisely, the nuclei are assumed to interact with the electrons through the potential

$$U(\bar{x}_1, \cdots, \bar{x}_M) = \inf \left\{ \langle \psi_e, H_e(\bar{x}_1, \cdots, \bar{x}_M) \cdot \psi_e \rangle, \quad \psi_e \in \mathcal{H}_e, \ \|\psi_e\| = 1 \right\} \qquad (2)$$

where H_e denotes the electronic Hamiltonian

$$H_e(\bar{x}_1, \cdots, \bar{x}_M) = -\sum_{i=1}^{N} \frac{1}{2} \Delta_{x_i} - \sum_{i=1}^{N} \sum_{k=1}^{M} \frac{z_k}{|x_i - \bar{x}_k(t)|} + \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|}.$$

Next, the nuclear motion is treated either as a quantum problem

$$i \frac{\partial \psi_n}{\partial t} = H_n \psi_n$$

with

$$H_n = -\sum_{k=1}^{M} \frac{1}{2\, m_k} \Delta_{\bar{x}_k} + U(\bar{x}_1, \cdots, \bar{x}_M) + \sum_{1 \leq k < l \leq M} \frac{z_k \, z_l}{|\bar{x}_k - \bar{x}_l|},$$

or as a semi-classical problem, or also, which is most frequently the case, as a classical problem. In the last case, the system reads

$$(A) \left\{ \begin{array}{l} m_k \dfrac{d^2 \bar{x}_k}{dt^2}(t) = -\nabla_{\bar{x}_k} \left(U(\bar{x}_1(t), \cdots, \bar{x}_M(t)) + \displaystyle\sum_{1 \leq l < m \leq M} \frac{z_l \, z_m}{|\bar{x}_l - \bar{x}_m|} \right) \\ U(\bar{x}_1, \cdots, \bar{x}_M) = \inf \left\{ \langle \psi_e, H_e(\bar{x}_1, \cdots, \bar{x}_M) \cdot \psi_e \rangle, \quad \psi_e \in \mathcal{H}_e, \ \|\psi_e\| = 1 \right\} \end{array} \right.$$

Let us remark that the adiabatic approximation is in fact the generalization of the Born-Oppenheimer approximation to a time-dependent setting (*see* [9] for details).

In practice, the minimization problem (2) has to be approximated, as in the time-independent case, by one of the standard (Hartree-Fock [10] or Density Functional [8]) method. However, problem (A) remains very time-consuming since a time-independent minimization problem has to be solved for each time step in order to compute ∇U. A possibility is to make an additional approximation first introduced by Car and Parrinello [6]: it consists in replacing the minimization problem by a fictitious (non-physical) electronic dynamics which makes the electronic wave function evolve in the neighbourhood of the adiabatic state. From a mathematical point of view, the Car-Parrinello method is investigated in [3].

2.3 A non-adiabatic approximation

Unfortunately, the adiabatic approximation is only valid under some physical assumptions for which we refer to [9]. In particular, when the electrons do not stay in a well-defined Born-Oppenheimer energy surface, this approximation cannot be used. This is the case for instance when a time-dependent electric field in turned on since this perturbation induces *a priori* transitions in the electronic spectrum.

In order to deal with such situations, the following approximation method is often used. Firstly, the nuclei are considered as classical point particles. In the sequel, this is refered to as the point nuclei approximation rather than, as often in Chemistry as the Born-Oppenheimer approximation, since, as underlined above, this is in fact the adiabatic approximation which is a direct extension of the original idea of Born and Oppenheimer. However, the physical justification of both the point nuclei and the Born-Oppenheimer approximations comes from the fact that nuclei are much heavier than electrons: the ratio is around 1836 for the hydrogen nucleus, and is greater than 10^4 for most of the atoms encountered in Chemistry. Consequently, the quantum nature of the nuclei can be neglected with good reason in most applications (let us recall that the tunnel effect transfer probability of a particle facing a potential barrier decreases exponentially with the mass of the particle). The point nuclei approximation is almost always valid in Chemistry (except for instance for studying specifically quantum phenomena involving nuclei as proton transfer by tunnel effect) and is therefore almost always used: the state of the system is then described at time t by

$$\left(\left\{ \bar{x}_k(t), \frac{d\bar{x}_k}{dt}(t) \right\}_{1 \leq k \leq M}, \psi_e(t) \right) \in \mathbb{R}^{6M} \times \bigwedge_{i=1}^{N} L^2(\mathbb{R}^3, \mathbb{C}^2),$$

where $\bar{x}_k(t)$ and $\frac{d\bar{x}_k}{dt}(t)$ denote respectively the position and the speed of the k-th nuclear at time t and where $\psi_e(t)$ denotes the electronic wave function at time t. The motion of the electrons is controlled by the electronic Schrödinger equation

$$i \frac{\partial \psi_e}{\partial t} = H_e(t)\, \psi_e, \tag{3}$$

where the electronic Hamiltonian reads

$$H_e(t) = -\sum_{i=1}^{N} \frac{1}{2} \Delta_{x_i} - \sum_{i=1}^{N} \sum_{k=1}^{M} \frac{z_k}{|x_i - \bar{x}_k(t)|} + \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|}$$

Notice that $H_e(t)$ acts on the electronic variables only; the nuclear coordinates $\bar{x}_k(t)$ are parameters. In some applications, the integration time scale of (3) is very small (say 10^{-15} s) and the motion of the nuclei can therefore be neglected: the nuclei remain fixed and the only equation to be solved is equation (3). In other applications, the motion of the nuclei play a crucial role. It is of course the case in chemical reactions. Such situations are most often described by the system consisting of (3) together with

$$m_k \frac{d^2 \bar{x}_k}{dt^2}(t) = -\nabla_{\bar{x}_k} W(t; \bar{x}_1(t), \cdots \bar{x}_M(t))$$

where

$$W(t; \bar{x}_1, \cdots, \bar{x}_M) = -\sum_{k=1}^{M} \int_{\mathbb{R}^3} \frac{z_k\, \rho(t,x)}{|x - \bar{x}_k|}\, dx + \sum_{1 \leq k < l \leq M} \frac{z_k\, z_l}{|\bar{x}_k - \bar{x}_l|}.$$

and $\rho(t,x) = N \int_{\mathbb{R}^{3(N-1)}} |\psi_e|^2(t, x, x_2, \cdots, x_N)\, dx_2 \cdots dx_N$ denotes the electronic density. The above two equations mean that each nucleus moves according to the Newton dynamics in the electrostatic potential created by the other nuclei and by the mean electronic density ρ. The term of electronic origin appearing in W is called the Hellman-Feynman potential; its expression is connected with the Ehrenfest Theorem (*see* [13] and also [2] for a mathematical argument).

The point nuclei approximation enables one to deal with the nuclear part of the system. Now, as in the time-independent setting, the electronic Schrödinger equation cannot be solved directly and additional approximations are necessary. We have chosen here to focus on the Hartree-Fock method which we briefly present here in a spinless context to simplify, so that here $\mathcal{H}_e = \bigwedge_{i=1}^N L^2(\mathbb{R}^3, \mathbb{C})$. Taking the spin into account make the notations more cumbersome but does not add any mathematical issue.

The Hartree-Fock approximation is of variational nature: it consists in forcing the wave function to move on the manifold

$$\mathcal{A} = \left\{ \psi_e(x_1, \cdots, x_n) = \frac{1}{\sqrt{N!}} \det(\phi_i(x_j)), \quad \phi_i \in H^1(\mathbb{R}^3, \mathbb{C}), \int_{\mathbb{R}^3} \phi_\mathrm{i} \cdot \phi_\mathrm{j}^* = \delta_\mathrm{ij} \right\}$$

of $\mathcal{H}_e$ and in replacing equation (3) by the stationarity condition for the action

$$\int_0^T \langle \psi_e(t), (i\partial_t \psi_e(t) - H_e(t)\psi_e(t)) \rangle \, dt.$$

The associated Euler-Lagrange equations [16] read

$$i\frac{\partial \phi_i}{\partial t} = \bar{H}_\Phi \phi_i + \sum_{j=1}^N \lambda_{ij} \phi_j$$

where $\bar{H}_\Phi$ is the Hartree-Fock Hamiltonian

$$\bar{H}_\Phi = -\frac{1}{2}\Delta + \sum_{k=1}^M \frac{z_k}{|\cdot - \bar{x}_k|} + \left(\sum_{i=1}^N |\phi_i|^2 \star \frac{1}{|x|} \right) - \sum_{j=1}^N \left(\phi_j^* \cdot \star \frac{1}{|x|} \right) \phi_j$$

and where the matrix $(\lambda_{ij}(t))$ is hermitian for any t. We draw the reader's attention on the fact that this approximation, which can be interpreted as a mean field approximation, has created nonlinearity: indeed the Hartree-Fock Hamiltonian depends on the electronic wave function. Contrary to what is often claimed in the Chemical literature, the $\lambda_{ij}(t)$ should not be interpreted as Lagrange multiplier associated with the constraints $\int_{\mathbb{R}^3} \phi_i \phi_j^* = \delta_{ij}$ (these constraints are automatically propagated by the dynamics because of the self-adjointness of the Hartree-Fock Hamiltonian), but rather as degrees of freedom associated with the gauge invariance $\phi_i(t) \longrightarrow U_{ij}(t)\phi_j(t)$ for any regular unitary $N \times N$ matrix valued function $t \mapsto U(t)$. In particular, this gauge invariance can be used to set the $\lambda_{ij}(t)$ to zero for all t so that the above system can be transformed into the simpler one

$$i\frac{\partial \phi_i}{\partial t} = \bar{H}_\Phi \phi_i. \tag{4}$$

Let us notice that the usual time-independent Hartree-Fock equations can be easily deduced from (4), like the time-independent Schrödinger equation is deduced from the time-dependent Schrödinger equation: indeed, let us search solutions of the form $\phi_i(t,x) = \phi_i(x)e^{-i\,\epsilon_i\,t}$; we thus obtain

$$\bar{H}_\Phi \cdot \phi_i = \epsilon_i \phi_i.$$

The time-independent Hartree-Fock method is a basic tool in Quantum Chemistry (*see* [10], [16] or any textbook of Quantum Chemistry). It has been deeply studied from a mathematical point of view, notably by Lieb and Simon [14] and Lions [15]. The time-dependent Hartree-Fock model has also been mathematically studied by Chadam and Glassey who proved in [7] the well-posedness of the Cauchy problem for fixed nuclei. Clearly, this assumption is too restrictive for the study of chemical reactions. Our first purpose consists in extending the Chadam and Glassey's result by including the nuclear dynamics into the evolution system.

The system under study couples the electronic Hartree-Fock evolution equation with the Hellman-Feynmann nuclear dynamics and reads:

$$(I)\left\{\begin{array}{l} i\dfrac{\partial \phi_i}{\partial t} = -\dfrac{1}{2}\Delta\phi_i - \displaystyle\sum_{k=1}^{M} \frac{z_k}{|\cdot - \bar{x}_k(t)|}\phi_i + \left(\sum_{j=1}^{N} |\phi_j|^2 \star \frac{1}{|x|}\right)\phi_i - \sum_{j=1}^{N}\left(\phi_j^* \phi_i \star \frac{1}{|x|}\right)\phi_j \\ m_k \dfrac{d^2 \bar{x}_k}{dt^2}(t) = -\nabla_{\bar{x}_k} W(t; \bar{x}_1(t), \cdots \bar{x}_M(t)) \\ \phi_i(0) = \phi_i^0, \quad \bar{x}_k(0) = \bar{x}_k^0, \quad \dfrac{d\bar{x}_k}{dt}(0) = \bar{v}_k^0. \end{array}\right.$$

with

$$W(t; \bar{x}_1, \cdots \bar{x}_M) = -\sum_{k=1}^{M}\sum_{i=1}^{N} \langle \phi_i(t) | \frac{z_k}{|\cdot - \bar{x}_k|} | \phi_i(t) \rangle + \sum_{1 \le k < l \le M} \frac{z_k\, z_l}{|\bar{x}_k - \bar{x}_l|}.$$

Let us notice that in calculations on large biological systems, the chemical system under consideration is sometimes split into two parts, the first one being computed with Quantum Mechanics, the other one with Classical Mechanics. The so-obtained systems are of the same nature as system (I) and therefore the results we obtain below also apply to them.

Our first purpose is to show that this Cauchy problem is well-posed, i.e. that system (I) has a unique global solution in a functional space to be made precise below, provided the ϕ_i^0 are chosen regular enough. This is the purpose of the next section. As far as we know, this problem has not yet been investigated.

3 The Cauchy problem for the isolated molecular system

In the sequel, L^p, $L^{p,r}$, H^s, and $C^{k,\alpha}$ without any additional argument denote respectively the Lebesgue, Lorentz, Sobolev, and Hölder spaces of $\mathbb{C}$-valued functions on $\mathbb{R}^3$. We also denote by C_u any real nonnegative universal constant (independent on the parameters of the problem) and by C_0 any real nonnegative constant depending on the parameters of the problem and in particular on the initial data.

For the sake of simplicity, the proofs presented in this section are performed on the example of the Helium atom (one nucleus and two electrons) in the Restricted Hartree-Fock formalism [10], [16]. However, it is important to note that our argument goes through *mutatis mutandis* in order to conclude for a system consisting of a finite number of nuclei and electrons in the Restricted or Unrestricted Hartree-Fock approximation [10]-[16]. In addition, we have rescaled the mass unit so that $m_e = 2$, in order to eliminate the factor $\frac{1}{2}$ in front of the Laplacian in the electronic Hamiltonian. The evolution equations under consideration thus reduce to

$$(II) \left\{ \begin{array}{l} i\dfrac{\partial\phi}{\partial t}(t,x) = -\Delta\phi(t,x) + V(x-\bar{x}(t))\phi(t,x) + \left(|\phi|^2 \star \dfrac{1}{|x|}\right)(t,x)\phi(t,x) \\ m\dfrac{d^2\bar{x}}{dt^2}(t) = \langle\phi(t)|\nabla V(\cdot - \bar{x}(t))|\phi(t)\rangle \\ \phi(0) = \phi^0, \quad \bar{x}(0) = \bar{x}^0, \quad \dfrac{d\bar{x}}{dt}(0) = \bar{v}^0. \end{array} \right.$$

where for any $t \geq 0$, $\phi(t) \in H^1$, $\|\phi^0\|_{L^2} = 1$ and $V(x) = -\frac{2}{|x|}$.

Our purpose is to show the

Theorem 1. *Suppose that $\phi^0 \in H^2$. Then, the system (II) has a unique global solution $(\phi, \bar{x})$ in*

$$X = (C^1([0,+\infty[, L^2) \cap C^0([0,+\infty[, H^2)) \times C^2([0,+\infty[, \mathbb{R}^3).$$

The rest of this section is devoted to the proof of the above theorem. This proof falls into three steps:

- subsection 3.2: existence of a local solution in

  $$X_\tau = (C^1([0,\tau], L^2) \cap C^0([0,\tau], H^2)) \times C^2([0,\tau], \mathbb{R}^3)$$

  for some $\tau > 0$ by a Schauder fixed point theorem;
- subsection 3.3: uniqueness of this local solution in the class X_τ;
- subsection 3.4: charge and energy conservation and H^2 estimate for concluding to global existence and uniqueness of the solution to (II) in X.

In fact, simpler proofs of each of these results may be obtained for the peculiar case of a one-nucleus system by a convenient change of coordinates. The advantage of the proof we have chosen to present here is that the results obtained in this way can be easily extended to cover the case of a more general chemical system made of many nuclei and electrons. We now state a more general result whose proof is a straightforward extension of the above proof and that we therefore leave to the reader.

Corollary 2. *Suppose that $\phi_i^0 \in H^2$ for all $1 \leq i \leq N$. Then, the system (I) has a unique global solution $(\{\phi_i\}_{1\leq i\leq N}, \{\bar{x}_k\}_{1\leq k\leq M})$ in*

$$X_{N,M} = (C^1([0,+\infty[, L^2) \cap C^0([0,+\infty[, H^2))^N \times (C^2([0,+\infty[, \mathbb{R}^3))^M.$$

Let us also mention that the smeared nuclei case is technically much simpler than the point nuclei case here examined. Indeed, the reader will notice that the main technical difficulties are due to the Coulomb singularity of the nuclear potential. All these technical difficulties may be therefore skipped in the "regular" case.

For the sake of clarity, we have regrouped the proofs of the main technical details in the following subsection.

3.1 A few technical lemmata

We begin with

Lemma 3. *Let us consider $\phi_1 \in H^2$ and $\phi_2 \in H^2$ and denote by*

$$f(\bar{x}) = \langle \phi_1 | \nabla V(\cdot - \bar{x}) | \phi_2 \rangle \qquad \textit{for any } \bar{x} \in \mathbb{R}^3.$$

Then $f \in C^1(\mathbb{R}^3, \mathbb{C}^3) \cap \mathrm{W}^{1,\infty}(\mathbb{R}^3, \mathbb{C}^3)$ and

$$\|f\|_{L^\infty} \leq 8 \|\nabla \phi_1\|_{L^2} \|\nabla \phi_2\|_{L^2},$$

$$\|Df\|_{L^\infty} \leq C_u \|\phi_1\|_{H^2} \|\phi_2\|_{H^2}.$$

Proof. The first inequality is a direct consequence of Cauchy-Schwarz and Hardy inequalities. Let us now consider the function

$$g(\bar{x}) = \langle \phi_1 | V(\cdot - \bar{x}) | \phi_2 \rangle = -2 \int_{\mathbb{R}^3} \frac{\phi_1(x)^* \phi_2(x)}{|x - \bar{x}|} \, dx,$$

which is defined and bounded in $\mathbb{R}^3$. Indeed,

$$|g(\bar{x})| \leq 2 \|\phi_1\|_{L^2} \| \frac{\phi_2(x)}{|x - \bar{x}|} \|_{L^2} \leq 4 \|\phi_1\|_{L^2} \|\nabla \phi_2\|_{L^2}.$$

As $\Delta g = 8\pi \phi_1^* \phi_2$ is in H^2 thus in $C^{0,\alpha}$ for all $0 < \alpha < 1/2$, we have by elliptic regularity results that $g \in C^{2,\alpha}$ for $0 < \alpha < 1/2$. In addition, the equality $g = -2\phi_1^* \phi_2 \star \frac{1}{|x|}$ with $\phi_i \in H^2$ implies that $g \in W^{2,\infty}$ (by a repeated use of Young inequality) with

$$\|g\|_{W^{2,\infty}} \leq C_u \|\phi_1 \phi_2^*\|_{H^2} \leq C_u \|\phi_1\|_{H^2} \|\phi_2\|_{H^2}.$$

Therefore, $f = -\nabla g$ belongs to $C^1(\mathbb{R}^3, \mathbb{C}^3) \cap \mathrm{W}^{1,\infty}(\mathbb{R}^3, \mathbb{C}^3)$ and

$$\|Df\|_{L^\infty} = \|D^2 g\|_{L^\infty} \leq C_u \|\phi_1\|_{H^2} \|\phi_2\|_{H^2}.$$

Let us now prove the existence of the propagator for the one-electron part of the Hartree-Fock Hamiltonian.

Lemma 4. *Let $\bar{x} \in C^1([0,T], \mathbb{R}^3)$ and $\{H(t)\}_{t \in [0,T]}$ the family of hamiltonians defined as*

$$H(t) = -\Delta + V(\cdot - \bar{x}(t)).$$

There exists a unique family of evolution operators $\{U(t,s),\ (t,s) \in [0,T] \times [0,T]\}$ such that

1. *$U(t,s)\,U(s,r) = U(t,r)$ for all $(t,s,r) \in [0,T]^3$;*

2. *$U(t,s)$ is unitary on L^2 for all $(t,s) \in [0,T] \times [0,T]$ and $(t,s) \mapsto U(t,s)$ is strongly continuous from $[0,T] \times [0,T]$ to $\mathcal{L}(L^2)$;*

3. *$U(t,s) \in \mathcal{L}(H^2)$ and for all $(t,s) \in [0,T] \times [0,T]$ and $(t,s) \mapsto U(t,s)$ is strongly continuous from $[0,T] \times [0,T]$ to $\mathcal{L}(H^2)$; moreover for all $C_0 > 0$ there exists $M_{T,C_0} > 0$ such that*

$$\left\| \frac{d\bar{x}}{dt} \right\|_{L^\infty(0,T;\mathbf{R}^3)} \le C_0 \quad \Rightarrow \quad \|U(t,s)\|_{\mathcal{L}(H^2)} \le M_{T,C_0} \quad \forall (t,s) \in [0,T]\times[0,T];$$

4. *the equalities $i\frac{dU(t,s)}{dt} = H(t)\,U(t,s)$ and $i\frac{dU(t,s)}{ds} = -U(t,s)\,H(s)$ hold strongly as equalities between operators from H^2 to L^2.*

Proof. This lemma is a consequence of a more general result by Yajima [22]. In order to stay as close as possible to the notations used in [22], we extend $\bar{x}$ to a function of class C^1 (still denoted by $\bar{x}$) defined on $[-T,T]$ and so that $\left\|\frac{d\bar{x}}{dt}\right\|_{L^\infty(-T,T)} = \left\|\frac{d\bar{x}}{dt}\right\|_{L^\infty(0,T)}$. It is clear that $\mathcal{V}(t,x) = V(x - \bar{x}(t))$ satisfies

$$\mathcal{V} \in C^0([-T,T],L^p) + C^0([-T,T],L^\infty), \qquad \frac{\partial \mathcal{V}}{\partial t} \in L^\infty(-T,T;L^{p_1}) + L^\infty(-T,T;L^\infty),$$

for $2 \le p < 3$ and $p_1 = 2p/(p+1)$. As proved in [22] this ensures the existence and the standard properties of the propagator for the family of Hamiltonians $\{H(t)\}_{t\in[-T,T]}$. For establishing the $\mathcal{L}(H^2)$-bound in statement 3, let us consider $\phi^0 \in H^2$ and $\phi(t) = U(t,0)\phi^0$. We have

$$\phi(t) = U_0(t)\phi^0 - i\int_0^t U_0(t-s)\mathcal{V}(s)\phi(s)\,ds,$$

with $U_0(t) = e^{it\Delta}$. Following [22], let us choose $2 \le p < 3$ and let us introduce for $\tau > 0$ the functional spaces

$$\mathcal{X}(\tau) = C^0([-\tau,\tau],L^2) \cap L^\theta(-\tau,\tau;L^q), \quad \mathcal{X}^*(\tau) = L^1(-\tau,\tau;L^2) + L^{\theta'}(\tau,\tau;L^{q'}),$$

$$\mathcal{Y}(\tau) = \left\{ u \in C^0([-\tau,\tau],H^2),\ \frac{\partial u}{\partial t} \in \mathcal{X}(\tau) \right\}, \quad \mathcal{Y}^*(\tau) = \left\{ u \in C^0([-\tau,\tau],L^2),\ \frac{\partial u}{\partial t} \in \mathcal{X}^*(\tau) \right\},$$

with $q = 2p/(p-1)$, $\theta = 4q/3(q-2)$, $1/q + 1/q' = 1$ and $1/\theta + 1/\theta' = 1$, equipped respectively with the norms

$$\|u\|_{\mathcal{X}(\tau)} = \|u\|_{C^0([-\tau,\tau],L^2)} + \|u\|_{L^\theta(-\tau,\tau;L^q)} \quad \|u\|_{\mathcal{X}^*(\tau)} = \|u\|_{L^1(-\tau,\tau;L^2) + L^{\theta'}(-\tau,\tau;L^{q'})},$$

$$\|u\|_{\mathcal{Y}(\tau)} = \|u\|_{C^0([-\tau,\tau],H^2)} + \|\frac{\partial u}{\partial t}\|_{\mathcal{X}(\tau)}, \quad \|u\|_{\mathcal{Y}^*(\tau)} = \|u\|_{C^0([-\tau,\tau],L^2)} + \|\frac{\partial u}{\partial t}\|_{\mathcal{X}^*(\tau)}.$$

We also define as in [22] the operator S by

$$(Su)(t) = \int_0^t U_0(t-s)u(s)\,ds.$$

The following estimates are proved in [22]:

- for all $v \in \mathcal{Y}^*(\tau)$, $S \cdot v \in \mathcal{Y}(\tau)$ and

$$\|S \cdot v\|_{\mathcal{Y}(\tau)} \leq C_u(1+\tau)\|v\|_{\mathcal{Y}^*(\tau)}, \tag{5}$$

- for any $\epsilon > 0$, there exists a constant C_ϵ such that for $\tau < 1/2$ and for all $u \in \mathcal{Y}(\tau)$, $\mathcal{V}u \in \mathcal{Y}^*(\tau)$ and

$$\|\mathcal{V}u\|_{\mathcal{Y}^*(\tau)} \leq \left(\epsilon\|\mathcal{V}\|_{\widetilde{\mathcal{M}}} + (2\tau)^{1-3/2p}\left\|\frac{\partial \mathcal{V}}{\partial t}\right\|_{\mathcal{N}}\right)\|u\|_{\mathcal{Y}(\tau)} + C_\epsilon\|\mathcal{V}\|_{\widetilde{\mathcal{M}}}\|u\|_{L^\infty(-\tau,\tau;L^2)} \tag{6}$$

with

$$\|\mathcal{V}\|_{\widetilde{\mathcal{M}}} = \|\mathcal{V}\|_{L^\infty(-\tau,\tau;L^p)+L^\infty(-\tau,\tau;L^\infty)}, \quad \left\|\frac{\partial \mathcal{V}}{\partial t}\right\|_{\mathcal{N}} = \left\|\frac{\partial \mathcal{V}}{\partial t}\right\|_{L^\infty(-\tau,\tau;L^{p_1})+L^\infty(-\tau,\tau;L^\infty)}$$

With these notations,

$$\phi(t) = U_0(t)\phi^0 - i(S\mathcal{V}\phi)(t).$$

Using inequalities (5) and (6), we obtain that for any $\epsilon > 0$ there exist a constant C_ϵ such that for $\tau \in]0, \min(1/2, T)[$,

$$\begin{aligned}
\|\phi\|_{\mathcal{Y}(\tau)} &\leq \|U_0(t)\phi^0\|_{\mathcal{Y}(\tau)} + \|S\mathcal{V}\phi\|_{\mathcal{Y}(\tau)} \\
&\leq C[\|\phi^0\|_{H^2} + (1+\tau)\|\mathcal{V}\phi\|_{\mathcal{Y}^*(\tau)}] \\
&\leq C\left[\|\phi^0\|_{H^2} + (1+\tau)\left((\epsilon\|\mathcal{V}\|_{\widetilde{\mathcal{M}}} + (2\tau)^{1/4}\left\|\frac{\partial \mathcal{V}}{\partial t}\right\|_{\mathcal{N}})\|\phi\|_{\mathcal{Y}(\tau)} + C_\epsilon\|\mathcal{V}\|_{\widetilde{\mathcal{M}}}\|\phi^0\|_{L^2}\right)\right],
\end{aligned}$$

where C does not depend on ϕ^0 and τ. But in this context, we have

$$\|V\|_{\widetilde{\mathcal{M}}} = \left\|\frac{2}{|x|}\right\|_{L^p+L^\infty} \quad \text{and} \quad \left\|\frac{\partial \mathcal{V}}{\partial t}\right\|_{\mathcal{N}} \leq \left\|\frac{d\bar{x}}{dt}\right\|_{L^\infty(-\tau,\tau)}\left\|\frac{2}{|x|^2}\right\|_{L^{p_1}+L^\infty}.$$

Therefore, as $\left\|\frac{d\bar{x}}{dt}\right\|_{L^\infty(-\tau,\tau)} \leq C_0$, one can find for $\epsilon > 0$ small enough a constant $0 < \tau < 1/2$ independent on ϕ^0 (τ depends however on C_0) such that there exists a constant C_{C_0} depending on C_0 but independent on ϕ^0 satisfying

$$\|\phi\|_{L^\infty(0,\tau;H^2)} \leq \|\phi\|_{\mathcal{Y}(\tau)} \leq C_{C_0}\|\phi^0\|_{H^2}.$$

Consequently, for $0 \leq t \leq \tau$, $\|U(t,0)\|_{\mathcal{L}(H^2)} \leq C_{C_0}$, and therefore from statement 1 of Lemma 4,

$$\|U(t,0)\|_{\mathcal{L}(H^2)} \leq C_{C_0}^{1+T/\tau} = M_{T,C_0}, \quad \forall t \in [0,T].$$

The same result holds for $U(t,s)$ with $(t,s) \in [0,T] \times [0,T]$.

We now turn to a detailed analysis of the nonlinear term appearing in the first equation of (II).

Lemma 5. *For $\phi \in H^1$, let us define*

$$F(\phi) = \left(|\phi|^2 \star \frac{1}{|x|}\right)\phi.$$

One has the following estimates

- *for $\phi \in H^1$ and $\psi \in H^1$,*

$$\|F(\phi) - F(\psi)\|_{L^2} \le C_u(\|\phi\|_{H^1}^2 + \|\psi\|_{H^1}^2)\|\phi - \psi\|_{L^2}, \tag{7}$$

- *there exists a constant C_F such that for all $\phi \in H^2$ and all $\psi \in H^2$*

$$\|F(\phi)\|_{H^2} \le C_F \, \|\phi\|_{H^1}^2 \|\phi\|_{H^2}, \tag{8}$$

$$\|F(\phi) - F(\psi)\|_{H^2} \le C_F(\|\phi\|_{H^2}^2 + \|\psi\|_{H^2}^2)\|\phi - \psi\|_{H^2}. \tag{9}$$

Proof. From Cauchy-Schwarz and Hardy inequalities, we have

$$\begin{aligned}
\|F(\phi) - F(\psi)\|_{L^2} &= \|(|\phi|^2 \star \frac{1}{|x|})\phi - (|\psi|^2 \star \frac{1}{|x|})\psi\|_{L^2} \\
&\le \|(|\phi|^2 \star \frac{1}{|x|})(\phi - \psi)\|_{L^2} + \|((|\phi|^2 - |\psi|^2) \star \frac{1}{|x|})\psi\|_{L^2} \\
&\le 2(\|\phi\|_{L^2}\|\nabla\phi\|_{L^2}\|\phi - \psi\|_{L^2} + \|\psi\|_{L^2}(\|\nabla\phi\|_{L^2} + \|\nabla\psi\|_{L^2})\|\phi - \psi\|_{L^2}) \\
&\le C_u(\|\phi\|_{H^1}^2 + \|\psi\|_{H^1}^2)\|\phi - \psi\|_{L^2},
\end{aligned}$$

which proves (7). Let us now establish (8) and (9). Firstly,

$$\|F(\phi)\|_{L^2} \le 2\|\nabla\phi\|_{L^2}\|\phi\|_{L^2}^2.$$

Next, for any arbitrary three functions a, b, and c in H^2, we have

$$\Delta\left[(a\,b \star \frac{1}{|x|})c\right] = 4\pi abc + 2(\nabla a\,b \star \frac{1}{|x|})\nabla c + 2(a\,\nabla b \star \frac{1}{|x|})\nabla c + (a\,b \star \frac{1}{|x|})\Delta c.$$

We thus obtain

$$\begin{aligned}
\left\|\Delta\left[(a\,b \star \frac{1}{|x|})c\right]\right\|_{L^2} &\le C_u(\|a\|_{L^6}\|b\|_{L^6}\|c\|_{L^6} + \|\nabla a\|_{L^2}\|\nabla b\|_{L^2}\|\nabla c\|_{L^2} \\
&\quad + \|a\|_{L^2}\|\nabla b\|_{L^2})\|\Delta c\|_{L^2} \\
&\le C_u\|a\|_{H^1}\|b\|_{H^1}\|c\|_{H^2}.
\end{aligned} \tag{10}$$

The inequality (8) follows. Finally,

$$\|F(\phi) - F(\psi)\|_{H^2}^2 = \|F(\phi) - F(\psi)\|_{L^2}^2 + \|\Delta(F(\phi) - F(\psi))\|_{L^2}^2,$$

and (7) provides us with a convenient upper bound of the first term of the right hand side. On the other hand,

$$\|\Delta(F(\phi)-F(\psi))\|_{L^2}^2 \le \|\Delta((|\phi|^2 \star \frac{1}{|x|})(\phi-\psi))\|_{L^2}^2 + \|\Delta(((|\phi|^2 - |\psi|^2) \star \frac{1}{|x|})\psi)\|_{L^2}^2.$$

Using (10), it is easy to conclude that

$$\|\Delta(F(\phi) - F(\psi))\|_{L^2}^2 \le C_u(\|\phi\|_{H^2}^2 + \|\psi\|_{H^2}^2)\|\phi - \psi\|_{H^2}.$$

Finally, we establish a somewhat unusual dispersion inequality for the free propagator, namely

Lemma 6. *Let $U_0(t) = e^{it\Delta}$ the propagator of the free particle. One has*

$$\|U_0(t)f\|_{L^{3,\infty}} \leq \frac{C_u}{\sqrt{t}}\|f\|_{L^{3/2,\infty}},$$

for all $f \in L^{3/2,\infty}$.

Proof. It is well-known (*see* [17] for instance) that for $2 \leq p \leq \infty$,

$$\|U_0(t)f\|_{L^p} \leq (2\pi|t|)^{-3/2+3/p}\|f\|_{L^{p'}}, \tag{11}$$

with $1/p + 1/p' = 1$, for all $f \in L^{p'}$. Let $0 < \epsilon \leq 1$. Inequality (11) is true in particular for $p_0 = 3+\epsilon$ and $p_1 = 3-\epsilon$. As $L^{p,p} = L^p$ (we recall that $L^{p,r}$ denote the Lorentz spaces), we thus can write

$$\|U_0(t)f\|_{L^{p_0,p_0}} \leq (2\pi|t|)^{-3/2+3/p_0}\|f\|_{L^{p_0',p_0'}},$$

$$\|U_0(t)f\|_{L^{p_1,p_1}} \leq (2\pi|t|)^{-3/2+3/p_1}\|f\|_{L^{p_1',p_1'}}.$$

Lemma 6 follows by using the general Marcinkiewicz interpolation theorem (*see* [1] p. 113 for instance) with $\theta = 1/2 - \epsilon/6$ so that

$$\frac{1-\theta}{p_0}+\frac{\theta}{p_1} = \frac{1}{3}, \quad \frac{1-\theta}{p_0'}+\frac{\theta}{p_1'} = \frac{1}{3/2}, \quad (1-\theta)\left(-\frac{3}{2}+\frac{3}{p_0}\right)+\theta\left(-\frac{3}{2}+\frac{3}{p_1}\right) = -\frac{1}{2}.$$

3.2 Local existence

As announced above, this subsection is devoted to the proof of a local-in-time existence result for the system (II). We begin by fixing some arbitrary time $T > 0$, and $0 < \tau \leq T$ such that

$$|\bar{v}^0| + \frac{16\,\tau}{m}M^2_{T,2|v^0|}\|\phi^0\|^2_{H^2} \leq 2|\bar{v}^0|, \tag{12}$$

$$8C_F M^3_{T,2|v^0|}\|\phi_0\|^2_{H^2}\tau < 1. \tag{13}$$

where we recall that the constant $M_{T,2|v^0|}$ is defined in Lemma 4, alinea 3 and the constant C_F in Lemma 5 alinea 2. We shall prove

Proposition 7. *The system (II) has a solution $(\phi, \bar{x})$ in*

$$X_\tau = (C^1([0,\tau], L^2) \cap C^0([0,\tau], H^2)) \times C^2([0,\tau], \mathbb{R}^3).$$

Proof. This result is obtained by a Schauder fixed point theorem. Let us denote by

$$\mathcal{B}^e_\tau = \left\{\psi \in C^1([0,\tau], L^2) \cap C^0([0,\tau], H^2) \quad / \quad \|\psi\|_{C^0([0,\tau],H^2)} \leq 2M_{T,2|v^0|}\,\|\phi^0\|_{H^2}\right\},$$

$$\mathcal{B}^n_\tau = \left\{\bar{y} \in C^1([0,\tau], \mathbb{R}^3) \quad / \quad \bar{y}(0) = \bar{x}^0,\ \frac{d\bar{y}}{dt}(0) = \bar{v}^0,\ \left\|\frac{d\bar{y}}{dt}\right\|_{C^0([0,\tau],\mathbb{R}^3)} \leq 2\,|\bar{v}^0|\right\}.$$

In the sequel, $\mathcal{B}_\tau^n$ is equipped with the topology of $C^1([0,\tau],\mathbb{R}^3)$ and $\mathcal{B}_\tau^e$ with the topology of $C^0([0,\tau],L^2)$. We shall need to consider the set $\mathcal{B}_\tau^n \cap C^2([0,\tau],\mathbb{R}^3)$ equipped with the topology of $C^2([0,\tau],\mathbb{R}^3)$. We shall also need the following two lemmata whose proofs are postponed untill the end of the proof of Proposition 7.

Lemma 8. *Let $\psi \in \mathcal{B}_\tau^e$. The equation*

$$m\frac{d^2\bar{z}}{dt^2}(t) = \langle\psi(t)|\nabla V(\cdot - \bar{z}(t))|\psi(t)\rangle \tag{14}$$

with initial data $\bar{z}(0) = \bar{x}^0$ and $\frac{d\bar{z}}{dt}(0) = \bar{v}^0$ has a unique solution in $C^2([0,\tau],\mathbb{R}^3)$ and this solution belongs to $\mathcal{B}_\tau^n$. Furthermore, the application

$$\begin{array}{rccc} \mathcal{F}\,:\, & \mathcal{B}_\tau^e & \longrightarrow & \mathcal{B}_\tau^n \cap C^2([0,\tau],\mathbb{R}^3) \\ & \psi & \mapsto & \bar{z} \end{array}$$

is continuous and bounded.

Lemma 9. *Let $\bar{y} \in \mathcal{B}_\tau^n$. The equation*

$$i\frac{\partial\psi}{\partial t}(t,x) = -\Delta\psi(t,x) + V(x-\bar{y}(t))\psi(t,x) + \left(|\psi|^2 \star \frac{1}{|x|}(t,x)\right)\psi(t,x) \tag{15}$$

with initial condition $\psi(0) = \phi^0$ has a unique solution ψ in $C^1([0,\tau],L^2) \cap C^0([0,\tau],H^2)$ and this solution is in $\mathcal{B}_\tau^e$. Furthermore, the application

$$\begin{array}{rccc} \mathcal{G}\,:\, & \mathcal{B}_\tau^n & \longrightarrow & \mathcal{B}_\tau^e \\ & \bar{y} & \mapsto & \psi \end{array}$$

is continuous and bounded.

Let us denote by i the compact injection

$$i\,:\,\mathcal{B}_\tau^n \cap C^2([0,\tau],\mathbb{R}^3) \longrightarrow \mathcal{B}_\tau^n.$$

In view of Lemmata 8 and 9 we can define the functional $\mathcal{K} = i \circ \mathcal{F} \circ \mathcal{G}$ which maps $\mathcal{B}_\tau^n$ into itself: if $\bar{y} \in \mathcal{B}_\tau^n$, $\bar{z} = \mathcal{K}(\bar{y})$ satisfies

$$\left\{\begin{array}{l} i\dfrac{\partial\psi}{\partial t}(t,x) = -\Delta\psi(t,x) + V(x-\bar{y}(t))\psi(t,x) + \left(|\psi|^2 \star \dfrac{1}{|x|}(t,x)\right)\psi(t,x) \\ m\dfrac{d^2\bar{z}}{dt^2}(t) = \langle\psi(t)|\nabla V(\cdot - \bar{z}(t))|\psi(t)\rangle \\ \psi(0) = \phi_0, \quad \bar{z}(0) = \bar{x}^0, \quad \dfrac{d\bar{z}}{dt}(0) = \bar{v}^0 \end{array}\right.$$

with $(\psi,\bar{z}) \in \mathcal{B}_\tau^e \times \mathcal{B}_\tau^n$.

The set $\mathcal{B}_\tau^n$ is convex and bounded and again from Lemmata 8 and 9, $\mathcal{K}$ is continuous and compact since

$$\mathcal{K}\,:\,\mathcal{B}_\tau^n \xrightarrow{\mathcal{G}} \mathcal{B}_\tau^e \xrightarrow{\mathcal{F}} \mathcal{B}_\tau^n \cap C^2([0,\tau],\mathbb{R}^3) \xhookrightarrow{i} \mathcal{B}_\tau^n,$$

the maps $\mathcal{F}$ and $\mathcal{G}$ being continuous and bounded and the injection i being continuous and compact. Then $\mathcal{K}$ has a fixed point $\bar{x}$ in $\mathcal{B}^n_\tau$, which is in fact also in $\mathcal{B}^n_\tau \cap C^2([0,\tau],\mathbb{R}^3)$ and $(\phi,\bar{x})$ with $\phi = \mathcal{F}(\bar{x})$ is a solution to (II) in $\mathcal{B}^e_\tau \times (\mathcal{B}^n_\tau \cap C^2([0,\tau],\mathbb{R}^3)) \subset X_\tau$. Proving Proposition 7 therefore amounts to proving Lemmata 8 and 9.

Proof of Lemma 8. For equation (14) to have a unique solution in $C^2([0,\tau],\mathbb{R}^3)$, suffices it to prove that the function

$$f(t,\bar{x}) = \langle \psi(t)|\nabla V(\cdot - \bar{x})|\psi(t)\rangle$$

is continuous, bounded and locally Lipschitz in $\bar{x}$. From Lemma 5, $f(t,\bar{x})$ is C^1 in $\bar{x}$ for all $t \in [0,\tau]$ and

$$\|f(t)\|_{W^{1,\infty}(\mathbb{R}^3,\mathbb{R}^3)} \leq C_u \|\psi\|^2_{C^0([0,\tau],H^2)}.$$

In particular, f is bounded and Lipschitz in $\bar{x}$ with a uniform Lipschitz constant on $[0,\tau]\times\mathbb{R}^3$. Besides, by considering a sequence $(t_n,\bar{x}_n)_{n\in\mathbf{N}}$ in $[0,\tau]\times\mathbb{R}^3$ that converges towards $(t,\bar{x})$ in $[0,\tau]\times\mathbb{R}^3$, we obtain

$$\begin{aligned}
|f(t_n,\bar{x}_n) - f(t,\bar{x})| &\leq |f(t,\bar{x}_n) - f(t,\bar{x})| + 2\int_{\mathbf{R}^3} \frac{||\psi(t_n,x)|^2 - |\psi(t,x)|^2|}{|x-\bar{x}_n|^2}\,dx \\
&\leq |f(t,\bar{x}_n) - f(t,\bar{x})| + 16\|\nabla\psi\|_{L^\infty(0,\tau;L^2)}\|\nabla(\psi(t_n) - \psi(t))\|_{L^2},
\end{aligned}$$

which implies that f is continuous since $f(t,\bar{x})$ is continuous with respect to $\bar{x}$ and $\psi \in C^0([0,\tau],H^1)$. Next, as $\psi \in \mathcal{B}^e_\tau$, we have

$$\sup_{[0,\tau]\times\mathbf{R}^3} |f| \leq 8\,\|\nabla\psi\|^2_{C^0([0,\tau],L^2)} \leq 16\, M^2_{T,2|v^0|}\,\|\phi^0\|^2_{H^2}$$

and thus in view of equation (12)

$$\left\|\frac{d\bar{z}}{dt}\right\|_{C^0([0,\tau],\mathbf{R}^3)} \leq |\bar{v}^0| + \frac{\tau}{m}\sup_{[0,\tau]\times\mathbf{R}^3}|f| \leq 2|\bar{v}^0|.$$

Then, $\mathcal{F}(\psi) \in \mathcal{B}^n_\tau$. Next, $\mathcal{F}$ is bounded since for any $\psi \in \mathcal{B}^e_\tau$, $\bar{x} = \mathcal{F}(\psi)$ is bounded in $C^2([0,\tau],\mathbb{R}^3)$ by a constant independent on ψ: indeed $\frac{d^2\bar{x}}{dt^2} = \frac{f}{m}$ with f bounded by $16\, M^2_{T,2|v^0|}\,\|\phi^0\|^2_{H^2}$. Finally, we prove the continuity of $\mathcal{F}$. Let us consider $\psi \in \mathcal{B}^e_\tau$ and a sequence $(\psi_n)_{n\in\mathbf{N}}$ in $\mathcal{B}^e_\tau$ converging towards ψ in $\mathcal{B}^e_\tau$ (for the topology of $C^0([0,\tau],L^2)$). Denoting by $\bar{x}_n = \mathcal{F}(\psi_n)$, $\bar{x} = \mathcal{F}(\psi)$, $\widetilde{\psi}_n = \psi_n - \psi$ and $\widetilde{x}_n = \bar{x}_n - \bar{x}$, we obtain

$$\begin{aligned}
m\frac{d^2\widetilde{x}_n}{dt^2}(t) &= \langle \psi_n(t)|\nabla V(\cdot - \bar{x}_n(t))|\psi_n(t)\rangle - \langle \psi(t)|\nabla V(\cdot - \bar{x}(t))|\psi(t)\rangle \\
&= \langle \psi(t)|\nabla V(\cdot - \bar{x}(t))|\widetilde{\psi}_n(t)\rangle + \langle \widetilde{\psi}_n(t)|\nabla V(\cdot - \bar{x}_n(t))|\psi_n(t)\rangle \\
&\quad + \langle \psi(t)|\nabla V(\cdot - \bar{x}_n(t))|\psi_n(t)\rangle - \langle \psi(t)|\nabla V(\cdot - \bar{x}(t))|\psi_n(t)\rangle.
\end{aligned}$$

Then, using Lemma 3, we obtain for all $t \in [0,\tau]$

$$\left| m\frac{d^2\widetilde{x}_n}{dt^2}(t)\right| \leq a_n + b_n|\widetilde{x}_n(t)|$$

with

$$a_n = \sup_{t\in[0,\tau]} \left(|\langle\psi(t)|\nabla V(\cdot-\bar{x}(t))|\widetilde{\psi}_n(t)\rangle| + |\langle\widetilde{\psi}_n(t)|\nabla V(\cdot-\bar{x}_n(t))|\psi_n(t)\rangle|\right)$$

and

$$0 \leq b_n \leq C_u \|\psi\|_{C^0([0,\tau],H^2)} \|\psi_n\|_{C^0([0,\tau],H^2)}$$

Now (b_n) is bounded since ψ_n and ψ are in $\mathcal{B}_\tau^e$ and (a_n) goes to zero when n goes to infinity: indeed, as the elements of $\mathcal{B}_\tau^e$ are bounded in $C^0([0,\tau],H^2$ and therefore in $C^0([0,\tau],L^2)\cap C^0([0,\tau],L^\infty)$, one can find C_0 such that for any $0<\epsilon\leq 1$,

$$\begin{aligned}
a_n &= 2 \sup_{\bar{x}\in\mathbb{R}^3,\, t\in[0,\tau]} \left(\int_{|x-\bar{x}|<\epsilon} \frac{|\psi(t,x)|\,|\widetilde{\psi}_n(t,x)|}{|x-\bar{x}|^2}\,dx + \int_{|x-\bar{x}|\geq\epsilon} \frac{|\psi(t,x)|\,|\widetilde{\psi}_n(t,x)|}{|x-\bar{x}|^2}\,dx \right) \\
&\leq C_0\epsilon + \frac{C_0}{\epsilon^2}\|\widetilde{\psi}_n\|_{C^0([0,\tau],L^2)} \leq 2C_0\epsilon
\end{aligned}$$

for n large enough. As $\widetilde{x}_n(0) = \frac{d\widetilde{x}_n}{dt}(0) = 0$, it follows from Gronwall Lemma that $\widetilde{x}_n$ goes to zero in $C^2([0,\tau],\mathbb{R}^3)$ when n goes to infinity.

Proof of Lemma 9. This proof is based on Lemma 4 which ensures the existence and the $\mathcal{L}(H^2)$-bounds of the propagator $U(t,s)$ for the family of Hamiltonians $H(t) = -\Delta + V(x-\bar{y}(t))$ and on the fact that the functional $F(\phi) = (|\phi|^2 \star \frac{1}{|x|})\phi$ is locally Lipschitz in H^2 (*see* Lemma 5). Indeed, using statement 3 of Lemma 4 and inequality (9), one can check that the functional

$$\psi \mapsto U(\cdot,0)\phi^0 - i\int_0^{\cdot} U(\cdot,s)F(\psi(s))\,ds$$

is a strict contraction in the Banach space $C^0([0,\tau],H^2)$ which maps $\mathcal{B}_\tau^e$ into itself for $\bar{y}\in\mathcal{B}_\tau^n$ and τ chosen according to (13). A standard application of the Picard fixed point theorem gives the existence and uniqueness of the solution to

$$(M) \qquad \phi(t) = U(t,0)\phi^0 - i\int_0^t U(t,s)F(\phi(s))\,ds,$$

in $C^0([0,\tau],H^2)$. Next, we have for $0\leq t,t'\leq\tau$, $t\neq t'$,

$$\begin{aligned}
\frac{1}{t'-t}(\phi(t')-\phi(t)) &= \frac{1}{t'-t}(U(t',0)-U(t,0))\phi^0 \\
&\quad -i\int_0^t \frac{1}{t'-t}(U(t',s)-U(t,s))F(\psi(s))\,ds \\
&\quad -i\frac{1}{t'-t}\int_t^{t'} U(t',s)F(\psi(s))\,ds,
\end{aligned}$$

and statements 3 and 4 of Lemma 4 enable us to pass to the limit $t'\longrightarrow t$ in L^2 in each term. We thus obtain that ϕ belongs to $C^1([0,\tau],L^2)$ and satisfies (15) in a strong sense. Besides, the solution to (15) with initial condition $\psi(0)=\phi^0$

is unique in the class $\mathcal{C}^1([0,\tau],L^2)\cap\mathcal{C}^0([0,\tau],H^2)$. Indeed let ψ_1 and ψ_2 be two solutions to (15) with $\psi_1(0)=\psi_2(0)=\phi^0$. We have $(\psi_1-\psi_2)(0)=0$ and a straightforward calculations shows that

$$\frac{d}{dt}\|\psi_1-\psi_2\|_{L^2}^2 = 2\,\mathrm{Im}\langle F(\psi_1)-F(\psi_2)|\psi_1-\psi_2\rangle_{L^2}.$$

Then, using (7), we obtain on $[0,\tau]$

$$\frac{d}{dt}\|\psi_1-\psi_2\|_{L^2}^2 \le C_u(\|\psi_1\|_{C^0([0,\tau],H^1)}+\|\psi_2\|_{C^0([0,\tau],H^1)})\|\psi_1-\psi_2\|_{L^2}^2$$

Uniqueness follows by Gronwall Lemma. Next, it is straightforward that $\mathcal{G}$ is bounded since the target set $\mathcal{B}_\tau^e$ is bounded. To conclude this section we have to prove that $\mathcal{G}$ is continuous. For that, let us consider a sequence $(\bar{y}_n)_{n\in\mathbf{N}}$ in $\mathcal{B}_\tau^n$ converging towards $\bar{y}$ in $\mathcal{B}_\tau^n$ and denote by $\psi_n=\mathcal{G}(\bar{x}_n)$, $\psi=\mathcal{G}(\bar{x})$, $\widetilde{\psi}_n=\psi_n-\psi$, $\widetilde{y}_n=\bar{y}_n-\bar{y}$. We have

$$i\frac{\partial\widetilde{\psi}_n}{\partial t} = -\Delta\widetilde{\psi}_n+V(\cdot-\bar{y})\widetilde{\psi}_n+(|\psi|^2\star\frac{1}{|x|})\widetilde{\psi}_n+\mathrm{Re}((\psi_n+\psi)^*\widetilde{\psi}_n\star\frac{1}{|x|})\psi_n+(V(\cdot-\bar{y}_n)-V(\cdot-\bar{y}))\psi_n.$$

Then denoting by $U(t,s)$ the unitary propagator associated with the family of Hamiltonians $H(t)=-\Delta+V(\cdot-\bar{x})+(|\psi|^2\star\frac{1}{|x|})$ we obtain

$$\widetilde{\psi}_n(t) = -i\int_0^t U(t,s)\left(\mathrm{Re}((\psi_n(s)+\psi(s))^*\widetilde{\psi}_n(s)\star\frac{1}{|x|})\psi_n(s)+(V(\cdot-\bar{y}_n(s))-V(\cdot-\bar{y}(s)))\psi_n(s)\right)ds.$$

Therefore, we have

$$\|\widetilde{\psi}_n(t)\|_{L^2}\le C_0\int_0^t(\|(V(\cdot-\bar{y}_n(s))-V(\cdot-\bar{y}(s)))\psi_n(s)\|_{L^2}+\|\widetilde{\psi}_n(s)\|_{L^2})\,ds.$$

As ψ_n is bounded in $L^\infty(0,\tau;L^2)$ and also in $L^\infty(0,\tau;L^\infty)$, we have

$$\|(V(\cdot-\bar{y}_n)-V(\cdot-\bar{y}))\psi_n\|_{L^\infty(0,\tau;L^2)}\underset{n\to+\infty}{\longrightarrow}0.$$

Then $\widetilde{\psi}_n$ goes to zero in $C^0([0,\tau],L^2)$ by Gronwall Lemma.

3.3 Uniqueness

The purpose of this section is to prove the

Proposition 10. The solution $(\phi,\bar{x})$ to (II) is unique in the class

$$X_\tau=(C^1([0,\tau],L^2(\mathbb{R}^3))\cap C^0([0,\tau],H^2(\mathbb{R}^3)))\times C^2([0,\tau],\mathbb{R}^3).$$

Proof. We claim that Proposition 10 follows from

Lemma 11. *Let $(\phi_1,\bar{x}_1)\in X_\tau$ and $(\phi_2,\bar{x}_2)\in X_\tau$ two solutions of (II) and denote by $\widetilde{x}=\bar{x}_1-\bar{x}_2$ and $\widetilde{\phi}=\phi_1-\phi_2$. Then there exists a constant C_0 depending only on $\|\phi_1\|_{C^0([0,\tau],H^2)}$ and $\|\phi_2\|_{C^0([0,\tau],H^2)}$ such that for all t in $[0,\tau]$,*

$$\left|\frac{d^2\widetilde{x}}{dt^2}(t)\right| \leq C_0\left(|\widetilde{x}(t)| + \|\widetilde{\phi}(t)\|_{L^{3,\infty}}\right) \tag{16}$$

$$\|\widetilde{\phi}(t)\|_{L^{3,\infty}} \leq C_0 \int_0^t \frac{1}{\sqrt{s}}\left(|\widetilde{x}(s)| + \|\widetilde{\phi}(s)\|_{L^{3,\infty}}\right) ds. \tag{17}$$

Indeed, let us assume for the moment that Lemma 11 is proved and consider the nonnegative continuous function on $[0,\tau]$

$$h(t) = \left(|\widetilde{x}(t)| + \|\widetilde{\phi}(t)\|_{L^{3,\infty}}\right)^p.$$

with $p > 2$. From inequalities (16) and (17), we deduce for all $t \in [0,\tau]$

$$\begin{aligned}
h(t) &\leq \left(C_0 \int_0^t [(t-s) + \frac{1}{\sqrt{s}}](|\widetilde{x}(s)| + \|\widetilde{\phi}(s)\|_{L^{3,\infty}})\, ds\right)^p \\
&\leq C_0^p \left(\int_0^t [(t-s) + \frac{1}{\sqrt{s}}]^{p'}\, ds\right)^{p/p'} \left(\int_0^t h(s)\, ds\right) \\
&\leq C_p \int_0^t h(s)\, ds,
\end{aligned}$$

where the constant $C_p < +\infty$ depends on p, τ, $\|\phi_1\|_{C^0([0,\tau],H^2)}$ and $\|\phi_2\|_{C^0([0,\tau],H^2)}$. As $h(0) = 0$, we obtain $h(t) = 0$ for all $t \in [0,\tau]$ from Gronwall Lemma. Uniqueness follows. There remains now to prove Lemma 11.

Proof of Lemma 11. Let $t \in [0,\tau]$. We have

$$\begin{aligned}
m\frac{d^2\widetilde{x}}{dt^2}(t) &= \langle\phi_1(t)|\nabla V(\cdot - \bar{x}_1(t))|\phi_1(t)\rangle - \langle\phi_2(t)|\nabla V(\cdot - \bar{x}_2(t))|\phi_2(t)\rangle \\
&= \langle\phi_1(t) - \phi_2(t)|\nabla V(\cdot - \bar{x}_1(t))|\phi_1(t)\rangle + \langle\phi_2(t)|\nabla V(\cdot - \bar{x}_1(t))|\phi_1(t)\rangle \\
&\quad + \langle\phi_2(t)|\nabla V(\cdot - \bar{x}_2(t))|\phi_1(t) - \phi_2(t)\rangle - \langle\phi_2(t)|\nabla V(\cdot - \bar{x}_2(t))|\phi_1(t)\rangle \\
&= \langle\phi_2(t)|\nabla V(\cdot - \bar{x}_1(t))|\phi_1(t)\rangle - \langle\phi_2(t)|\nabla V(\cdot - \bar{x}_2(t))|\phi_1(t)\rangle \\
&\quad + \langle\phi_2(t)|\nabla V(\cdot - \bar{x}_2(t))|\widetilde{\phi}(t)\rangle + \langle\widetilde{\phi}(t)|\nabla V(\cdot - \bar{x}_1(t))|\phi_1(t)\rangle.
\end{aligned}$$

On the one hand we deduce from Lemma 3 that the function $(t,\bar{x}) \mapsto \langle\phi_2(t)|\nabla V(\cdot - \bar{x})|\phi_1(t)\rangle$ is Lipschitz in the second variable with Lipschitz constant bounded by $C_u\|\phi_1(t)\|_{H^2}\|\phi_2(t)\|_{H^2}$ and on the other hand, we have

$$|\langle\phi|\nabla V(\cdot - \bar{x})|\widetilde{\phi}(t)\rangle| \leq C_u\|\phi\|_{H^2}\|\widetilde{\phi}(t)\|_{L^{3,\infty}},$$

for $\phi \in H^2$ and $\bar{x} \in \mathbb{R}^3$. This proves (16). Let us now turn to the estimate (17) on $\widetilde{\phi}$. We can write

$$\begin{aligned}
\widetilde{\phi}(t) &= -i\int_0^t U_0(t-s)\Big[V(x - \bar{x}_1(s))\widetilde{\phi}(s) + (V(x - \bar{x}_1(s)) - V(x - \bar{x}_2(s)))\phi_2(s) \\
&\qquad + (|\phi_1(s)|^2 \star \frac{1}{|x|})\widetilde{\phi}(s) + ((|\phi_1(s)|^2 - |\phi_2(s)|^2) \star \frac{1}{|x|})\phi_2(s)\Big]\, ds,
\end{aligned}$$

where $U_0(t) = e^{it\Delta}$ denotes as above the free particle propagator which satisties (*see* Lemma 6) the estimate

$$\|U_0(t)f\|_{L^{3,\infty}} \le \frac{C_u}{\sqrt{t}}\|f\|_{L^{3/2,\infty}},$$

for all $f \in L^{3/2,\infty}$. Thus,

$$\begin{aligned}
\|\widetilde{\phi}(t)\|_{L^{3,\infty}} \quad \le \quad & \int_0^t \frac{C_u}{\sqrt{t}} \Big[\|V(\cdot - \bar{x}_1(s))\widetilde{\phi}(s)\|_{L^{3/2,\infty}} + \|(V(\cdot - \bar{x}_1(s)) - V(\cdot - \bar{x}_2(s)))\phi_2(s)\|_{L^{3/2,\infty}} \\
& \|(|\phi_1(s)|^2 \star \frac{1}{|x|})\widetilde{\phi}(s)\|_{L^{3/2,\infty}} + \|((|\phi_1(s)|^2 - |\phi_2(s)|^2) \star \frac{1}{|x|})\phi_2(s)\|_{L^{3/2,\infty}} \Big] \, ds.
\end{aligned}$$

Now, omitting the time-dependence in order to lighten the notations

$$\|V(\cdot - \bar{x}_1)\widetilde{\phi}\|_{L^{3/2,\infty}} \le C_u \left\| \frac{2}{|x|} \right\|_{L^{3,\infty}} \|\widetilde{\phi}\|_{L^{3,\infty}},$$

$$\begin{aligned}
\|(V(\cdot - \bar{x}_1) - V(\cdot - \bar{x}_2))\phi_2\|_{L^{3/2,\infty}} \quad & \le \quad \|(V(\cdot - \widetilde{x}) - V(\cdot))\phi_2(\cdot + \bar{x}_2)\|_{L^{3/2,\infty}} \\
& \le \quad \left\| \left| \frac{2}{|x - \widetilde{x}|} - \frac{2}{|x|} \right| |\phi_2(x + \bar{x}_2)| \right\|_{L^{3/2,\infty}} \\
& \le \quad \left\| \frac{2|\widetilde{x}|}{|x|\,|x - \widetilde{x}|} |\phi_2(x + \bar{x}_2)| \right\|_{L^{3/2,\infty}} \\
& \le \quad 2 \left\| \frac{|\phi_2(x + \bar{x}_2)|}{|x|\,|x - \widetilde{x}|} \right\|_{L^{3/2,\infty}} |\widetilde{x}| \\
& \le \quad C_u \|\phi_2\|_{L^\infty} \left\| \frac{1}{|x|} \right\|_{L^{3,\infty}}^2 |\widetilde{x}|,
\end{aligned}$$

$$\begin{aligned}
\|(|\phi_1|^2 \star \frac{1}{|x|})\widetilde{\phi}\|_{L^{3/2,\infty}} \quad & \le \quad C_u \left\| |\phi_1|^2 \star \frac{1}{|x|} \right\|_{L^{3,\infty}} \|\widetilde{\phi}\|_{L^{3,\infty}} \\
& \le \quad C_u \|\phi_1\|_{L^2}^2 \left\| \frac{1}{|x|} \right\|_{L^{3,\infty}} \|\widetilde{\phi}\|_{L^{3,\infty}},
\end{aligned}$$

$$\begin{aligned}
\|((|\phi_1|^2 - |\phi_2|^2) \star \frac{1}{|x|})\phi_2\|_{L^{3/2,\infty}} \quad & \le \quad \left\| \left(|\widetilde{\phi}|(|\phi_1| + |\phi_2|) \star \frac{1}{|x|} \right) |\phi_2| \right\|_{L^{3/2,\infty}} \\
& \le \quad C_u \left\| \left(|\widetilde{\phi}|(|\phi_1| + |\phi_2|) \star \frac{1}{|x|} \right) \right\|_{L^{6,2}} \|\phi_2\|_{L^2} \\
& \le \quad C_u \||\widetilde{\phi}|(|\phi_1| + |\phi_2|)\|_{L^{6/5,2}} \left\| \frac{1}{|x|} \right\|_{L^{3,\infty}} \|\phi_2\|_{L^2} \\
& \le \quad C_u (\|\phi_1\|_{L^2} + \|\phi_2\|_{L^2})\|\phi_2\|_{L^2} \left\| \frac{1}{|x|} \right\|_{L^{3,\infty}} \|\widetilde{\phi}\|_{L^{3,\infty}},
\end{aligned}$$

(*see* [23] for instance for a proof of the Young inequality in the Lorentz spaces).
The estimate on $\widetilde{\phi}$ follows.

3.4 Global existence

We now conclude the proof of Theorem 1. As we have already established the local existence and uniqueness of the solution to (II) in X_τ for some $\tau > 0$, the global existence is equivalent to the existence of locally uniform estimates on $|\bar{x}(t)|$, $\left|\frac{d\bar{x}}{dt}(t)\right|$ and $\|\phi(t)\|_{H^2}$ (*see* Segal [19]).

Let us consider T^* such that (II) has a unique solution in X_τ for all $\tau < T^*$.

Firstly, the conservation of the L^2-norm of ϕ is a consequence of the self-adjointness of the (nonlinear) electronic Hamiltonian and can be established by computing the derivative $\frac{d}{dt}\|\phi(t)\|^2_{L^2}$. We leave this calculation to the reader. Thus, for all $t \in [0, T^*[$, we have

$$\|\phi(t)\|_{L^2} = \|\phi^0\|_{L^2} = 1.$$

Secondly, the total energy

$$E(t) = \frac{m}{2}\left|\frac{d\bar{x}}{dt}(t)\right|^2 + \int_{\mathbf{R}^3} |\nabla\phi(t)|^2 + \int_{\mathbf{R}^3} V(x-\bar{x}(t))|\phi|^2(t,x)\,dx + \frac{1}{2}\mathcal{D}(|\phi(t)|^2, |\phi(t)|^2)$$

where $D(u,v) = \int_{\mathbf{R}^3}\int_{\mathbf{R}^3} \frac{u(x)\,v(y)}{|x-y|}\,dx\,dy$, is conserved. Therefore there exists a constant C_0 depending only on the initial data such that for all $t \in [0, T^*[$,

$$\left|\frac{d\bar{x}}{dt}(t)\right| \leq C_0,$$

$$\int_{\mathbf{R}^3} |\nabla\phi(t)|^2 \leq C_0.$$

We additionally conclude from the above first equation a bound on $|\bar{x}(t)|$. Now, for $t \in [0, T^*[$,

$$\begin{aligned}
\|\phi(t)\|_{H^2} &\leq \|U(t,0)\phi^0\|_{H^2} + \int_0^t \|U(t,s)F(\phi(s))\|_{H^2}\,ds \\
&\leq M_{T^*,C_0}\left(\|\phi^0\|_{H^2} + C_F(1+C_0^2)\int_0^t \|\phi(s)\|_{H^2}\,ds\right).
\end{aligned}$$

Therefore, by Gronwall Lemma, there exist two constants a and b depending only on the initial data such that

$$\|\phi(t)\|_{H^2} \leq a\,e^{b\,t}$$

for all $t \in [0, T^*[$. The global existence and uniqueness follow.

4 The Cauchy problem for the molecular system subjected to a external uniform time-dependent electric field

When an external time-dependent uniform electric field $\mathcal{E}(t)$ is turned on, the molecular Hamiltonian H given by (1) is modified by the addition of the external electric potential $\mathcal{V}(t,x) = -\sum_{k=1}^{M} z_k \mathcal{E}(t)\cdot \bar{x}_k + \sum_{i=1}^{N} \mathcal{E}(t)\cdot x_i$ created by the field.

In the present section, our purpose is to show that the Cauchy problem examined in this previous section, namely that corresponding to the non-adiabatic approximation with a Hartree-Fock electronic dynamics coupled with a classical Hellman-Feynman type nuclear dynamics, is still well posed when the molecule is subjected to an external uniform time-dependent electric field. As mentioned in the introduction, this situation appears in particular in the modelling of laser control of chemical reactions.

We leave open the interesting questions concerning the long-time behavior of the system when the electric field is time-independent. When nuclei are fixed and for a linear electronic Schrödinger equation (in other words, when the electronic Hamiltonian is linear and time-independent) we know from the R.A.G.E. Theorem and its corollaries that the electronic wave function leaves the region of the nuclei and does not return (*see* [18] for details). We do not know what happens when nuclei are allowed to move and/or when the electronic Hamiltonian is nonlinear, except that there exists no stationary state (*see* [5]). Nevertheless, it seems to us reasonable to conjecture that all the nuclei move towards the region of negative infinite potential while the electronic cloud moves towards the region of positive infinite potential. We hope that this observation will stimulate further research.

As above, we reason about the system describing the Helium atom in the Restricted Hartree-Fock approximation but, again as in the previous section, our argument can easily be extended to a molecular system consisting of a finite number of electrons and nuclei. In presence of an external time-dependent uniform electric field, system (II) becomes

$$(IIe)\left\{\begin{array}{l} i\dfrac{\partial\phi}{\partial t} = -\Delta\phi + V(\cdot-\bar{x}(t))\phi + \mathcal{E}(t)\cdot x\,\phi + \left(|\phi|^2\star\dfrac{1}{|x|}\right)\phi \\ m\dfrac{d^2\bar{x}}{dt^2}(t) = \langle\phi(t)|\nabla V(\cdot-\bar{x}(t))|\phi(t)\rangle + z\mathcal{E}(t) \\ \phi(0)=\phi^0, \quad \bar{x}(0)=\bar{x}^0, \quad \dfrac{d\bar{x}}{dt}(0)=\bar{v}^0. \end{array}\right.$$

The domain of the self-adjoint operator

$$\bar{H}_\phi(t) = -\Delta + V(\cdot-\bar{x}(t)) + \mathcal{E}(t)\cdot x + \left(|\phi(t)|^2\star\frac{1}{|x|}\right)$$

contains $H^2_{ef} = \left\{\phi\in H^2(\mathbb{R}^3) \quad / \quad \sqrt{1+|x|^2}\,\phi\in L^2(\mathbb{R}^3)\right\}$ if $\mathcal{E}(t)\neq 0$ and equals H^2 in the special case when $\mathcal{E}(t)=0$. The space H^2_{ef} is a Hilbert space when equipped with the norm

$$\|\phi\|_{H^2_{ef}} = \left(\|\sqrt{1+|x|^2}\,\phi\|^2_{L^2} + \|\Delta\phi\|^2_{L^2}\right)^{1/2}.$$

Let us now state and prove

Proposition 12. *Let $\mathcal{E}\in C^0([0,+\infty[,\mathbb{R}^3)$. If $\phi^0\in H^2_{ef}$, the system (IIe) has a unique global solution $(\phi,\bar{x})$ in*

$$Y = (C^1([0,+\infty[, L^2) \cap C^0([0,+\infty[, H^2_{ef})) \times C^2([0,+\infty[, \mathbb{R}^3).$$

The following lemma is useful for establishing the proof of the above Proposition.

Lemma 13. *Let $\psi \in C^0([0,+\infty[, L^2)$, $\alpha \in C^0([0,+\infty[, \mathbb{R})$, $\beta \in C^0([0,+\infty[, \mathbb{R}^3)$, $f \in C^0([0,+\infty[, \mathbb{R})$, and $g \in C^0([0,+\infty[, \mathbb{R}^3)$. Denote by*

$$\zeta(t,x) = f(t) e^{i[\alpha(t)+\beta(t)\cdot x]} \psi(t, x + g(t)).$$

Then $\zeta \in C^0([0,+\infty[, L^2)$.

Proof. Suffices it to prove the continuity at $t_0 = 0$. In order to lighten the notations, we assume that $f(0) = 1$, $g(0) = 0$, $\alpha(0) = 0$ and $\beta(0) = 0$. Let $0 \le t \le 1$. We have

$$\begin{aligned}
\|\zeta(t) - \zeta(0)\|_{L^2} &= \|f(t)e^{i[\alpha(t)+\beta(t)\cdot x]}\psi(t, x+g(t)) - \psi(0,x)\|_{L^2} \\
&\le \|f(t)e^{i[\alpha(t)+\beta(t)\cdot x]}(\psi(t, x+g(t)) - \psi(0, x+g(t)))\|_{L^2} \\
&\quad + \|f(t)e^{i[\alpha(t)+\beta(t)\cdot x]}(\psi(0, x+g(t)) - \psi(0,x))\|_{L^2} \\
&\quad + \|(f(t)e^{i[\alpha(t)+\beta(t)\cdot x]} - 1)\psi(0,x)\|_{L^2} \\
&\le C_0\|\psi(t) - \psi(0)\|_{L^2} + C_0\|\psi(0, x+g(t)) - \psi(0,x)\|_{L^2} \\
&\quad + \|(f(t)e^{i[\alpha(t)+\beta(t)\cdot x]} - 1)\psi(0,x)\|_{L^2}.
\end{aligned}$$

As $\psi \in C^0([0,+\infty[, L^2)$, we have

$$\|\psi(t) - \psi(0)\|_{L^2} \underset{t\to 0}{\longrightarrow} 0.$$

Besides, in view of Lebesgue convergence theorem,

$$\|(f(t)e^{i[\alpha(t)+\beta(t)\cdot x]} - 1)\psi(0,x)\|_{L^2} \underset{t\to 0}{\longrightarrow} 0.$$

Finally, let $\epsilon > 0$, $R \ge 1$ and $N \ge 0$, such that denoting by $\psi_N(t,x) = \max(\psi(t,x), N)$, one has

$$\int_{|x|\ge R-1} |\psi(0,x)|^2 \, dx \le \epsilon/4 \quad \text{and} \quad \int_{\mathbb{R}^3} |\psi_N(0,x) - \psi(0,x)|^2 \, dx \le \epsilon/4.$$

As from Lebesgue convergence theorem

$$\int_{|x|<R} |\psi_N(0, x+g(t)) - \psi_N(0,x)|^2 \underset{t\to 0}{\longrightarrow} 0,$$

one can find $\tau > 0$ such that for any $0 \le t \le \tau$,

$$\|\psi(0, x+g(t)) - \psi(0,x)\|^2_{L^2} \le \epsilon.$$

This concludes the proof of the continuity of ζ at $t_0 = 0$ in $C^0([0,+\infty[, L^2)$.

Proof of Proposition 12. Uniqueness. Firstly, let us assume that (II_e) has a solution in Y. Following [11], we define

$$\chi(t,x) = e^{i[k(t)+h(t)\cdot x]}\phi(t,x-2G(t)), \quad \bar{y}(t) = \bar{x}(t) + 2G(t),$$

with $h(t) = \int_0^t \mathcal{E}(s)\,ds$, $G(t) = \int_0^t h(s)\,ds$ and $k(t) = \int_0^t |h|^2(s)\,ds - 2h(t)\cdot G(t)$. The evolution equations satisfied by $(\chi, \bar{y})$ read

$$(\widetilde{II_e}) \left\{ \begin{array}{l} i\dfrac{\partial \chi}{\partial t} = -\Delta\chi + V(\cdot - \bar{y}(t))\chi + \left(|\chi|^2 \star \dfrac{1}{|x|}\right)\chi \\ m\dfrac{d^2\bar{y}}{dt^2}(t) = \langle \chi(t)|\nabla V(\cdot - \bar{y}(t))|\chi(t)\rangle + (z+2m)\mathcal{E}(t) \\ \chi(0) = \phi_0, \ \bar{y}(0) = \bar{x}^0, \ \dfrac{d\bar{y}}{dt}(0) = \bar{v}^0. \end{array} \right.$$

Clearly, $\bar{y} \in C^2([0,+\infty[,\mathbb{R}^3)$ and, using Lemma 13, a straighforward calculation shows that $\chi \in C^0([0,+\infty[,H^2)$. Inserting this result in the first equation in $(\widetilde{II_e})$, we obtain in addition $\frac{\partial\chi}{\partial t} \in C^0([0,+\infty[,L^2)$. Consequently, $(\chi,\bar{y}) \in X$. The same argument as in Section 3.3 shows that the solution to $(\widetilde{II_e})$ in X is unique. Therefore, if it exists, the solution to (II_e) is unique.

Existence. Following the same strategy as in Section 3.2, it can be proved that system $(\widetilde{II_e})$ actually has a solution $(\chi,\bar{y})$ in X (the drift term $(z+2m)\mathcal{E}$ does not bring up any additional difficulty). Besides, $\sqrt{1+|x|^2}\chi \in C^0([0,+\infty[,L^2)$. Indeed, let us consider the function $\eta(x) = \sqrt{1+|x|^2}$, which satisfies

$$\nabla\eta(x) = \frac{x}{(1+|x|^2)^{1/2}} \in L^\infty \quad \text{and} \quad \Delta\eta(x) = -\frac{3+2\,|x|^2}{(1+|x|^2)^{3/2}} \in L^\infty,$$

and a monotonic sequence $(\eta_n)_{n\in\mathbb{N}}$ of non-negative functions in $\mathcal{D}(\mathbb{R}^3)$ such that

- η_n, $\nabla\eta_n$, and $\Delta\eta_n$ converge a.e. towards η, $\nabla\eta$, and $\Delta\eta$ respectively;
- $\eta_n \le \eta$, $|\nabla\eta_n| \le 2|\nabla\eta|$ and $|\Delta\eta_n| \le 2|\Delta\eta|$.

Clearly, for any $n \in \mathbb{N}$, $\xi_n(t,x) = \eta_n(x)\,\chi(t,x)$ is in $C^0([0,+\infty[,H^2)$ and satisfies the following equation

$$\xi_n(t) = U(t,0)\,\xi_n(0) - i\int_0^t U(t,s) f_n(s)\,ds,$$

where $U(t,s)$ is the propagator associated with the family of Hamiltonians $H(t) = -\Delta + V(\cdot - \bar{y}(t)) + \left(|\chi|^2 \star \frac{1}{|x|}\right)$ and where

$$f_n(t,x) = 2\nabla\eta_n(x)\cdot\nabla\chi(t,x) + \Delta\eta_n(x)\,\chi(t,x).$$

Denoting by $\xi(t,x) = \eta(x)\,\chi(t,x)$ and $f(t,x) = 2\nabla\eta(x)\cdot\nabla\chi(t,x) + \Delta\eta(x)\,\chi(t,x)$, it follows from the convergences

$$\xi_n(0) \underset{n\to+\infty}{\longrightarrow} \xi(0) \quad \text{in } L^2 \quad \text{and} \quad f_n \underset{n\to+\infty}{\longrightarrow} f \quad \text{in } C^0([0,+\infty[,L^2)$$

that ξ satisfies

$$\xi(t) = U(t,0)\,\xi(0) - i\int_0^t U(t,s)f(s)\,ds,$$

wich implies in particular that $\xi \in C^0([0,+\infty[, L^2)$.

Finally, denoting by

$$\phi(t,x) = e^{-i[k(t)+h(t)\cdot(x+2\,G(t))]}\chi(t,x+2G(t)),$$

$$\bar{x}(t) = \bar{y}(t) - 2G(t).$$

and using again Lemma 13, it is easy to conclude that $(\phi,\bar{x})$ is in Y and satisfies (II_e) in a strong sense.

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