J. Math. Pures Appl. 105 (2016) 1–30

Contents lists available at ScienceDirect

Journal de Mathématiques Pures et Appliquées

www.elsevier.com/locate/matpur

# Kinetic energy estimates for the accuracy of the time-dependent Hartree–Fock approximation with Coulomb interaction

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ARTICLE INFO

*Article history:*
Received 9 June 2015
Available online 8 September 2015

*MSC:*
35Q40
35Q55
81Q05

*Keywords:*
Hartree–Fock
Many-body theory
Mean-field limit for fermions

ABSTRACT

We study the time evolution of a system of $N$ spinless fermions in $\mathbb{R}^3$ which interact through a pair potential, e.g., the Coulomb potential. We compare the dynamics given by the solution to Schrödinger's equation with the time-dependent Hartree–Fock approximation, and we give an estimate for the accuracy of this approximation in terms of the kinetic energy of the system. This leads, in turn, to bounds in terms of the initial total energy of the system.



RÉSUMÉ

On étudie l'évolution temporelle d'un système de $N$ fermions sans spin dans $\mathbb{R}^3$ qui interagissent via un potentiel à deux particules, par exemple, le potentiel de Coulomb. On compare la solution de l'équation de Schrödinger avec son approximation donnée par la méthode de Hartree–Fock dépendant du temps, et on estime la précision de cette approximation en fonction de l'énergie cinétique du système. De ceci découle une borne de l'erreur en fonction de l'énergie totale du système.



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http://dx.doi.org/10.1016/j.matpur.2015.09.003

## 1. Introduction

*The model.* In quantum mechanics, the state of a system of $N$ identical particles is described by a wave function $\Psi_t$ which evolves in time $t \in \mathbb{R}$ according to Schrödinger's equation,

$$\begin{cases} i\partial_t \Psi_t = H\Psi_t \,, \\ \Psi_{t=0} = \Psi_0 \,. \end{cases} \tag{1}$$

Given the (Bose–Einstein or Fermi–Dirac) particle statistics and the one-particle Hilbert space $\mathfrak{h}$, the wave function $\Psi_t$ is a normalized vector in $\mathfrak{H}_b^{(N)} := \mathcal{S}^{(N)}[\mathfrak{h}^{\otimes N}]$, for a system of $N$ bosons, or in $\mathfrak{H}_f^{(N)} := \mathcal{A}^{(N)}[\mathfrak{h}^{\otimes N}]$, for a system of $N$ fermions. Here $\mathcal{S}^{(N)}$ and $\mathcal{A}^{(N)}$ are the orthogonal projections onto the totally symmetric and the totally antisymmetric subspace, respectively, of the $N$-fold tensor product $\mathfrak{h}^{\otimes N}$ of the one-particle Hilbert space $\mathfrak{h}$. The dynamics (1) is generated by the Hamilton operator $H$ which is self-adjointly realized on a suitable dense domain in $\mathfrak{H}_b^{(N)}$ or $\mathfrak{H}_f^{(N)}$, respectively.

In the present article we study a system of $N$ spinless fermions in $\mathbb{R}^3$, so $\Psi_t \in \mathfrak{H}_f^{(N)}$, and $\mathfrak{h} = L^2[\mathbb{R}^3]$ is the space of square-integrable functions on $\mathbb{R}^3$. The Hamiltonian is given by

$$H \;=\; \nu + \sum_{j=1}^{N} h_j^{(1)} + \lambda \sum_{1\le j<k\le N} v(x_j - x_k) \,, \tag{2}$$

where

- the number $\nu \in \mathbb{R}$ is a constant contribution to the total energy. For example, if we describe a molecule in the Born–Oppenheimer approximation, then $\nu$ would account for the nuclear–nuclear repulsion,
- the coupling constant $\lambda > 0$ is a small parameter and possibly depends on the particle number $N \geq 1$ (while our interest ultimately lies in the description of systems with $N \gg 1$, the estimates in this article hold for any $N \geq 1$),
- the self-adjoint operator $h^{(1)}$ on $\mathfrak{h}$ is of the form $-a\Delta + w(x)$, where $a > 0$ and the external potential $w$ is an infinitesimal perturbation of the Laplacian,
- and $v(x) := \pm|x|^{-1}$ is the Coulomb potential, for $x \in \mathbb{R}^3 \setminus \{0\}$; $v(x) = +|x|^{-1}$ is the repulsive case, $v(x) = -|x|^{-1}$ the attractive case.

The Hamiltonian specified in (2) describes several situations of interest, e.g.:

- **Atom.** For an atom in the $(0^{th})$ Born–Oppenheimer approximation with a nucleus of charge $Z$ at the origin, we have repulsive interaction and

$$\nu = 0 \,, \quad h^{(1)} = -\frac{\Delta}{2} - \alpha\frac{Z}{|x|} \,, \quad \lambda = \alpha \,, \tag{3}$$

  where $\alpha > 0$ is the fine structure constant whose physical value is $\alpha \simeq 1/137$. Note that our system of units is chosen such that the reduced Planck constant $\hbar$, the electron mass $m$ and the speed of light $c$ are equal to one, and the charge of the electron is $-e = -\sqrt{\alpha}$. For more details about this choice of units see [45, p. 21].
- **Molecule.** More generally, we can consider a molecule with $M \in \mathbb{N}$ nuclei of charges $Z_1, \ldots, Z_M > 0$ at fixed, distinct positions $R_1, \ldots, R_M \in \mathbb{R}^3$ in the Born–Oppenheimer approximation. In this case we have

$$\nu = \sum_{1\le m<l\le M} \frac{\alpha Z_m Z_l}{|R_m - R_l|} \,, \quad h^{(1)} = -\frac{\Delta}{2} - \sum_{m=1}^{M} \frac{\alpha Z_m}{|x - R_m|} \,, \quad \lambda = \alpha \,. \tag{4}$$