Semi-Classical Limit Theorems for Hartree-Fock Theory

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Abstract. Consider a large number of electrons with Coulomb repulsion moving under the influence of static nuclei. It is assumed the potentials due to the nuclei are Coulombic away from their centers but are smooth at the centers, so no singularities exist. The author shows that the exchange energy for the Hartree-Fock ground state of this system converges in a suitable limit to the formula obtained by Dirac for exchange energy as an integral of the one body density.

Introduction

In this paper we prove some semi-classical limit theorems for the Hartree-Fock theory associated with a Coulombic Hamiltonian of electrons interacting with static nuclei. We assume there are \( k \) nuclei with positive charges \( z_j, 1 \leq j \leq k \), situated at the points \( R_j \in \mathbb{R}^3, 1 \leq j \leq k \), respectively. Let \( g : \mathbb{R}^3 \to \mathbb{R} \) be a continuous nonnegative spherically symmetric function with compact support whose integral over \( \mathbb{R}^3 \) is 1. We assume the electrostatic potential at \( x \in \mathbb{R}^3 \) due to the nuclei is

\[
V(x) = \sum_{j=1}^{k} z_j \int_{\mathbb{R}^3} \frac{g(y-R_j)}{|x-y|} \, dy.
\] (1.1)

Thus for large \( x \) the potential \( -V(x) \) is the same as the Coulombic potential due to the \( k \) nuclei, but for \( x \) close to the points \( R_j, 1 \leq j \leq k \), \( V(x) \) is smoothed. Ideally we would like to assume simply that \( V(x) \) is the Coulomb potential due to the \( k \) nuclei. However the techniques of this paper do not apply to that case.

Next we introduce \( n \) electrons, each with charge \( -1 \) and mass \( m \), moving in the field of the potential \( -V(x) \). Let \( x_i \in \mathbb{R}^3 \times \{-1, 1\} = \Omega \) be the coordinate of the \( i^{th} \) electron in the product of \( \mathbb{R}^3 \) with the spin space \( \{-1, 1\} \). Then the \( n \) electron wave function \( \psi \) may be written as \( \psi = \psi(x_1, \ldots, x_n) \), where \( \psi \in L^2(\Omega^n) \). Let \( H_n \) be the

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Hilbert space of all such \( \psi \) which are anti-symmetric in the \( x_i, 1 \leq i \leq n \). By the Pauli exclusion principle \( \mathcal{H}_n \) is the state space for the \( n \) electron system. The corresponding Hamiltonian \( H_n(V) \) is given by

\[
H_n(V) = -\hbar^2(8\pi^2m)^{-1} \sum_{i=1}^{n} \Delta_i + \sum_{i=1}^{n} V(x_i) + \sum_{i<j=1}^{n} |x_i - x_j|^{-1},
\]

with \( \hbar \) being Planck’s constant, and \( \Delta_i \) the Laplacian in the \( x_i \) variable \( 1 \leq i \leq n \).

Here we are concerned with estimating asymptotically the ground state energy \( E_n(V) \) of the \( n \) electron system as \( n \to \infty \). If \( [ , ] \) denotes the inner product on \( \mathcal{H}_n \), then the Rayleigh-Ritz procedure yields

\[
E_n(V) = \inf\{ [\psi, H_n(V)\psi] : \psi \in \mathcal{H}_n, ||\psi|| = 1 \}. \tag{1.3}
\]

Let \( z \) be defined by

\[
z = \sum_{j=1}^{k} z_j. \tag{1.4}
\]

It is known \[14\] that if \( n \leq z \) there is a function \( \psi \in \mathcal{H}_n \) which achieves the infimum in (1.2). This function is not necessarily unique.

In Hartree-Fock (HF) theory one takes the infimum in (1.3) over functions \( \psi \) which are anti-symmetric products of single electron wave functions. Let \( \psi_1(x), \ldots, \psi_n(x) \) be an orthonormal set in \( L^2(\Omega) \) representing the wave functions of the \( n \) electrons and \( \psi \) the Slater determinant of the \( \psi_1, \ldots, \psi_n \). Then

\[
[\psi, H_n(V)\psi] = e_{HF}(\psi_1, \ldots, \psi_n), \tag{1.5}
\]

where

\[
e_{HF} = K + A + R + E_x. \tag{1.6}
\]

The kinetic energy \( K \) is given by

\[
K(\psi_1, \ldots, \psi_n) = \hbar^2(8\pi^2m)^{-1} \sum_{i=1}^{n} \int_{\Omega} |\nabla \psi_i(x)|^2 \, dx. \tag{1.7}
\]

The attractive and repulsive potential energies \( A \) and \( R \) may be expressed as integrals of the one body density

\[
\rho(x) = \sum_{i=1}^{n} |\psi_i(x)|^2, \quad x \in \Omega. \tag{1.8}
\]

Thus we have

\[
A(\rho, V) = -\int_{\Omega} \rho(x) V(x) \, dx, \tag{1.9}
\]

\[
R(\rho) = \frac{1}{2} \int_{\Omega} \int_{\Omega} \frac{\rho(x)\rho(y)}{|x-y|} \, dx \, dy. \tag{1.10}
\]

The nonclassical exchange energy \( E_x \) is given by

\[
E_x(\psi_1, \ldots, \psi_n) = -\frac{1}{2} \int_{\Omega} \int_{\Omega} \frac{|\sum_{i=1}^{n} \psi_i(x)\psi_i(y)|^2}{|x-y|} \, dx \, dy. \tag{1.11}
\]