Commun. Math. Phys. 88, 133–150 (1983)

Communications in Mathematical Physics

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, $1 \leqq j \leqq k$, situated at the points $R_j \in \mathbb{R}^3$, $1 \leqq j \leqq k$, 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 $-V(x)$, where

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

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, $1 \leqq j \leqq k$, $V(x)$ 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 ψ may be written as $\psi \equiv \psi(x_1, \ldots, x_n)$, where $\psi \in L^2(\Omega^n)$. Let $\mathcal{H}_n$ be the

* Research supported by NSF Grant No. MCS 8100761