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The Hartree-Fock Theory for Coulomb Systems

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Abstract. For neutral atoms and molecules and positive ions and radicals, we prove the existence of solutions of the Hartree-Fock equations which minimize the Hartree-Fock energy. We establish some properties of the solutions including exponential falloff.

§ 1. Introduction

In this paper we discuss the Hartree (H) and Hartree-Fock (HF) theories associated with the purely Coulombic Hamiltonian of electrons interacting with static nucleii. Our purpose will be to prove that these theories exist (in the sense that the equations have solutions which minimize the H or HF energy) whenever the system has an excess positive charge after the removal of one electron. An announcement of these results was given in [22] and an outline of the proof was given in [19].

The precise quantum system is described by the Hamiltonian

$$H = -\sum_{i=1}^{N} \Delta_i + \sum_{i=1}^{N} V(x_i) + \sum_{i<j} |x_i - x_j|^{-1}\,, \tag{1}$$

where

$$V(x) = -\sum_{j=1}^{k} z_j |x - R_j|^{-1} \tag{2}$$

acting on the Hilbert space $\mathscr{H} = L^2_a(\mathbb{R}^{3N}; \mathbb{C}^{2^N})$. We assume $z_j > 0$, all j. The subscript a on L^2 indicates that we are to consider functions in L^2 as $\Psi(x_1, \sigma_1; \ldots; x_N, \sigma_N)$ with $x_i \in \mathbb{R}^3$, $\sigma_i \in \pm 1/2$ and only allow those Ψ antisymmetric under interchanges of i and j. The particles have two spin states, but we could allow q spin states in our analysis below with only notational changes. The physically correct Fermi statistics

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