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Error Bound for the Hartree–Fock Energy of Atoms and Molecules

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Abstract. We estimate the error of the Hartree–Fock energy of atoms and molecules in terms of the one-particle density matrix corresponding to the exact ground state. As an application we show this error to be of order $O(Z^{5/3-\delta})$ for any $\delta < 2/21$ as the total nuclear charge Z becomes large.

1. Introduction

The nonrelativistic quantum mechanical model for an atom ($K = 1$) or molecule is given by the Hamiltonian

$$H_N(\underline{Z}, \underline{R}) := \sum_{i=1}^{N} \left(-\Delta_i - \sum_{j=1}^{K} \frac{Z_j}{|x_i - R_j|} \right) + \sum_{1 \leqq i < j}^{N} \frac{1}{|x_i - x_j|}, \tag{1}$$

acting as a self-adjoint operator on a dense domain $D_N \subseteq \bigwedge_{i=1}^{N} (L^2(\mathbb{R}^3) \otimes \mathbb{C}^q)$. Here we regard the nuclei of charge Z_j as pointcharges at fixed positions R_j, for $1 \leqq j \leqq K$. For the sake of brevity we denote $\underline{Z} := (Z_1, \ldots, Z_K)$ and $\underline{R} := (R_1, \ldots, R_K)$. The nuclei are surrounded by N electrons of spin $s = \frac{q-1}{2}$, so, in nature $q = 2$. We are interested in the ground state energy

$$E_Q(N, \underline{Z}, \underline{R}) := \inf\{\langle \Psi_N | H_N(\underline{Z}, \underline{R}) | \Psi_N \rangle | \Psi_N \in D_N, \| \Psi_N \| = 1\}, \tag{2}$$

which coincides with the bottom of the spectrum of $H_N(\underline{Z}, \underline{R})$. (Henceforth $\| \Psi_N \| = 1$ is assumed without further notice.) In general, $E_Q(N, \underline{Z}, \underline{R})$ is inaccessible to direct computation. Here we are concerned with the asymptotic validity of approximate theories in the limit

$$Z \to \infty, \quad N \approx Z, \quad \underline{Z}/Z \text{ fixed}, \quad \min_{1 \leqq i < j \leqq K} |R_i - R_j| \geqq c Z^{-2/3+\varepsilon}. \tag{3}$$

To leading order $Z^{7/3}$, E_Q is given by the Thomas–Fermi energy E_{TF}, as was shown