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Accuracy of Mean Field Approximations for Atoms and Molecules

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Abstract. We estimate the accuracy of the mean field approximation induced by the Thomas–Fermi potential for the ground state energy of atoms and molecules. Taking the Dirac exchange correction into account, we show the error to be of the form $O(Z^{5/3-\delta}) + D$ for any $\delta < 2/231$ as the total nuclear charge Z becomes large. D is an electrostatic energy of the difference density that measures the deviation of the mean field ground state from self-consistency.

1. Introduction

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

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

acting as a self-adjoint operator on $D_N := \bigwedge_{i=1}^{N} \tilde{\mathscr{H}} \subseteq \mathscr{H}_N := \bigwedge_{i=1}^{N} \mathscr{H}$, $\mathscr{H} := L^2(\mathbb{R}^3) \otimes \mathbb{C}^m$, $\tilde{\mathscr{H}} := H^2(\mathbb{R}^3) \otimes \mathbb{C}^m$. Here, $\underline{Z} := (Z_1, \ldots, Z_K)$ and $\underline{R} := (R_1, \ldots, R_K)$ denote the charges and positions of the nuclei. We will drop this dependence in our notation henceforth. Unless stated otherwise, the operators are always assumed to act as identity on $\mathbb{C}^m$.

We are interested in approximations for the ground state energy

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

The most widely used one in physics is the *Mean Field* approximation. It consists in replacing the pair potential $\sum_{1 \leq i < j}^{N} \frac{1}{|x_i - x_j|}$ in (1) by an average one-body potential

$$\sum_{i=1}^{N} \int \frac{d^3 y}{|x_i - y|} \rho(y) - \frac{1}{2} D(\rho, \rho) , \tag{3}$$