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A Lower Bound on the Size of Molecules

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Abstract. We give lower bounds on the 'size' of a molecule in the Born–Oppenheimer approximation. For diatomic molecules, we give a new lower bound on the number of electrons in terms of the nuclear charges.

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1. Introduction

The nonrelativistic quantum mechanical model for a polyatomic molecule (in units in which $\hbar = 2m_e = e = 1$) is given by the Hamiltonian

$$H_N(\underline{Z}, \underline{R}) \equiv H_N(Z_1, \ldots, Z_K, R_1, \ldots, R_K)$$
$$\equiv \sum_{i=1}^{N} \left(-\Delta_i - \sum_{k=1}^{K} \frac{Z_k}{|x_i - R_k|} \right) + \sum_{1 \leqslant i < j \leqslant N} \frac{1}{|x_i - x_j|} +$$
$$+ \sum_{1 \leqslant l < m \leqslant K} \frac{Z_l Z_m}{|R_l - R_m|}$$

acting as a self-adjoint operator on a dense domain $D_N \subseteq \wedge_{i=1}^{N} (\mathbf{L}^2(\mathbf{R}^3) \otimes \mathbf{C}^q)$. Here, N and K denote the number of electrons and nuclei, respectively. We regard the nuclei as fixed (which corresponds to the Born–Oppenheimer approximation). The charge of the kth nucleus ($1 \leqslant k \leqslant K$) is denoted by $Z_k > 0$ and his position by $R_k \in \mathbf{R}^3$. We consider the spin to be given by $s = (q-1)/2$. In nature, $q = 2$ (i.e. $s = 1/2$).

The groundstate energy of the molecule is given by

$$E_N(\underline{Z}, \underline{R}) \equiv \inf\{ <\psi_N | H_N(\underline{Z}, \underline{R}) | \psi_N > | \psi_N \in D_N, \| \psi_N \| = 1 \},$$

which coincides with the bottom of the spectrum of $H_N(\underline{Z}, \underline{R})$.

Let us define the Born–Oppenheimer groundstate energy of a molecule as

$$E_N(\underline{Z}) \equiv \inf_{\underline{R}} E_N(\underline{Z}, \underline{R})$$

Following [11, 14], we say that the molecule defined by $(N, \underline{Z})$ has a stable bound state if the following conditions are satisfied:

(1) There is at least one configuration $\underline{R}_o$ such that $E_N(\underline{Z}) = E_N(\underline{Z}, \underline{R}_o)$ and $E_N(\underline{Z})$ is a discrete eigenvalue of $H_N(\underline{Z}, \underline{R}_o)$.
(2) $E_N(\underline{Z}) < \lim_{\lambda\to\infty} \inf\{E_N(\underline{Z}, \underline{R}) | \max_{l\neq m} |R_l - R_m| > \lambda\}$.

If a stable configuration $\underline{R}_o$ exists, then we can define 'the size' of the molecule as

$$R_o \equiv \max_{l\neq m} |R_{o_l} - R_{o_m}|.$$

In this Letter, we are interested in establishing lower bounds to the size of the molecules. In fact, we show that

$$R_o \geqslant \left(\frac{8}{3q^2}\right)^{1/3} \frac{\left(Z^2 - \sum_{i=1}^{K} Z_i^2\right)}{\left(Z^2 - \frac{1}{K}\sum_{i=1}^{K} Z_i^2\right)} N^{-1/3}$$

considering statistics or

$$R_o \geqslant 2\frac{\left(Z^2 - \sum_{i=1}^{K} Z_i^2\right)}{\left(Z^2 - \frac{1}{K}\sum_{i=1}^{K} Z_i^2\right)} \frac{1}{N}$$

without particle symmetry.

These bounds can be improved for diatomic molecules. In fact, for diatomic molecules, we prove (Theorem 2 below)

$$R \geqslant \frac{Z_1 Z_2}{(Z_1^2 + Z_2^2)} \frac{1}{-\varepsilon^N(0)}, \tag{1}$$

where $-\varepsilon^N(0) \leqslant N/4$ for bosons and $-\varepsilon^N(0) \leqslant \frac{1}{4}(12)^{1/3}N^{1/3}$ for fermions.

In our proof for diatomic molecules we will use the Feynman–Hellmann formula, the Virial Theorem and the Rayleigh–Ritz variational principle.

For diatomic molecules, Solovej [13] proved the bound

$$R \geqslant \frac{1}{3} \frac{1}{-\varepsilon^N(0)}. \tag{2}$$

Formula (1) is better for values of the nuclear charges such that $(3 - \sqrt{5})/2 \leqslant Z_1/Z_2 \leqslant (3 + \sqrt{5})/2$, in particular in the homopolar case we have

$$R \geqslant \frac{1}{2} \frac{1}{-\varepsilon^N(0)}.$$

For polyatomic molecules, Ruskai and Solovej [11] have also found some estimates on the size of molecules (see Section 2 below).