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A bound on the kinetic energy of diatomic molecules

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Abstract. We consider a diatomic molecule with fixed nuclei of charges Z_1 and Z_2 , and N electrons. We find upper bounds on the kinetic energy of the molecule and the energy of the electronic contribution as a function of the nuclear separation R .

1. Introduction

Consider a diatomic molecule with infinitely heavy nuclei of charges $Z_1, Z_2 > 0$ at positions $-R/2\hat{n}$ and $R/2\hat{n}$ respectively, and N electrons. Here \hat{n} is a fixed unitary vector in \mathbb{R}^3 . The electronic contribution (in units where $\hbar = 2m_e = e = 1$) is given by the Hamiltonian

$$H_N(Z_1, Z_2, R) = \sum_{i=1}^N \left(-\Delta_i - \frac{Z_1}{|x_i + (R/2)\hat{n}|} - \frac{Z_2}{|x_i - (R/2)\hat{n}|} \right) + \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|} \quad (1)$$

acting over the antisymmetric space $D_N \subseteq \wedge_{i=1}^N (\mathbb{L}^2(\mathbb{R}^3) \otimes \mathbb{C}^q)$. We consider the spin to be given by $s = (q - 1)/2$, where $q = 2$ in nature (i.e. $s = 1/2$).

The ground-state energy of the electronic contribution is defined by

$$e_N(Z_1, Z_2, R) = \inf\{\langle \varphi_N | H_N(Z_1, Z_2, R) | \varphi_N \rangle \mid \varphi_N \in D_N, \|\varphi_N\| = 1\} \quad (2)$$

while the kinetic energy is given by

$$K = \langle \phi_N | \sum_{i=1}^N -\Delta_i | \phi_N \rangle \quad (3)$$

where ϕ_N is the ground state of the electronic contribution. The total energy of the diatomic molecule is given by

$$E_N(Z_1, Z_2, R) = e_N(Z_1, Z_2, R) + \frac{Z_1 Z_2}{R}$$

where the second term corresponds to the nuclear repulsion energy.

Mathematical properties of the ground-state energy of the electronic contribution as a function of the nuclear separation are of general interest. Aventini and Seiler [1] have studied the Hamiltonian of a diatomic molecule with one electron proving that the eigenvalues depend smoothly on the distance between the nuclei. A diatomic molecule with more electrons was studied by Combes and Seiler [2]; they proved the analyticity of the eigenvalues of the electronic Hamiltonian for all $R \neq 0$. Lieb and Simon [3] have studied the dependence of the ground-state energy of the electronic contribution for a diatomic molecule with one electron as a function of the nuclear separation R , proving that

this function increases monotonically for $R > 0$. In that paper they conjectured that there also exists similar monotonicity properties for diatomic molecules with more electrons.

In this paper we will prove an upper bound on the electronic contribution of a diatomic molecule with N electrons. Also, we can give an upper bound on the derivative of the electronic contribution at $R = 0^+$.

In a beautiful work [4], Bach proved the accuracy of the ground-state energy in the Hartree–Fock theory. In that paper he obtained a simple bound on the kinetic energy for molecules, a bound which was later used by Ivrii and Sigal [5] in their proof of the Scott conjecture for molecules. In this work we want to show an improved bound for the kinetic energy of diatomic molecules using the virial theorem, the Feynman–Hellmann formula, the Rayleigh–Ritz variational characterization for atoms and a simple concavity argument. We have used these methods in [6] to improve the bounds given by Solovej on the size and on the number of electrons in a diatomic molecule [7].

The main results in this paper are the following theorems.

Theorem 1. For a diatomic molecule of nuclear charges $Z_1, Z_2 > 0$ and N electrons, the kinetic energy obeys

$$K \leq 2(Z_1 + Z_2)^2 \left\{ \frac{1 + 4(Z_1 + Z_2)R}{1 + 2(Z_1 + Z_2)R} \right\} (-\epsilon^N(0)) \quad (4)$$

where $\epsilon^N(0)$ is the ground-state energy of $\sum_{i=1}^N (-\Delta_i - |x_i|^{-1})$.

Remark. Since

$$\left\{ \frac{1 + 4(Z_1 + Z_2)R}{1 + 2(Z_1 + Z_2)R} \right\} \leq 2 \quad \text{for all } R \geq 0$$

it follows from (4) that

$$K \leq 4(Z_1 + Z_2)^2 (-\epsilon^N(0)) \quad (5)$$

which corresponds to the bound given by Bach [4].

In the case when $N = 1$, we can improve the bound given above:

Theorem 2. For a diatomic molecule of nuclear charges $Z_1, Z_2 > 0$ and one electron, the kinetic energy is bounded by

$$K \leq -E_1^{\text{at}}(Z_1 + Z_2) = \frac{1}{4}(Z_1 + Z_2)^2 \quad (6)$$

where $E_N^{\text{at}}(Z)$ is the ground-state energy of an atom with N electrons and nuclear charge Z .

Notice that, because of the virial theorem, $-E_1^{\text{at}}(Z_1 + Z_2)$ is the kinetic energy of an atom with nuclear charge $(Z_1 + Z_2)$ and one electron. Then, for a diatomic molecule with one electron we have

$$K(\text{molecule}) \leq K(\text{atom}). \quad (7)$$

We believe this inequality should also hold for systems with more electrons.

In the following section we will obtain an upper bound on the electronic contribution in the manner of the united atom bound [8]. In section 3 we will prove the theorems and in the last section we will give an application of these theorems in obtaining an upper bound on the electronic density at the nuclei.

2. An upper bound on the energy of the electronic contribution

The united atom bound [8] for the electronic contribution to the energy of a diatomic molecule of nuclear charges $Z_1, Z_2 > 0$ and nuclear separation R is

$$e_N(Z_1, Z_2, R) \geq E_{\text{at}}(N, Z_1 + Z_2) \tag{8}$$

where $E_{\text{at}}(N, Z)$ is the ground-state energy of an atom of nuclear charge Z and N electrons.

It is also possible to obtain an upper bound on $e_N(Z_1, Z_2, R)$ in terms of $E_{\text{at}}(N, Z_1 + Z_2)$. In fact, we have the following lemma.

Lemma 1.

$$E_{\text{at}}(N, Z_1 + Z_2) \leq e_N(Z_1, Z_2, R) \leq (1 + 2(Z_1 + Z_2)R)^{-1} E_{\text{at}}(N, Z_1 + Z_2) \tag{9}$$

Proof. The lower bound above is the united atom bound. To prove the upper bound let $e(R) = e_N(Z_1, Z_2, R)$ and ϕ_N on the ground state of $H_N(Z_1, Z_2, R)$. We define $x \equiv (x_1, \dots, x_i, \dots, x_N) \in \mathbb{R}^{3N}$, where $x_i \in \mathbb{R}^3$. Therefore, we can write

$$H_N(Z_1, Z_2, R) = -\Delta + V_R(x)$$

where $\Delta = \sum_{i=1}^N \Delta_i$ is the Laplacian operator over \mathbb{R}^{3N} and

$$V_R(x) = \sum_{i=1}^N \left(-\frac{Z_1}{|x_i + (R/2)\hat{n}|} - \frac{Z_2}{|x_i - (R/2)\hat{n}|} \right) + \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|}.$$

Since $e(R)$ is non-degenerate [2, 9, 10], we can use the Feynman–Hellmann formula

$$\begin{aligned} \frac{\partial e(R)}{\partial R} &= \langle \phi_N | \frac{\partial V_R(x)}{\partial R} | \phi_N \rangle \\ &= \langle \phi_N | \sum_{i=1}^N \left(\frac{Z_1 \hat{n} \cdot (x_i + (R/2)\hat{n})}{2|x_i + (R/2)\hat{n}|^3} - \frac{Z_2 \hat{n} \cdot (x_i - (R/2)\hat{n})}{2|x_i - (R/2)\hat{n}|^3} \right) | \phi_N \rangle \\ &\leq \langle \phi_N | \sum_{i=1}^N \left(\frac{Z_1}{2|x_i + (R/2)\hat{n}|^2} + \frac{Z_2}{2|x_i - (R/2)\hat{n}|^2} \right) | \phi_N \rangle \\ &= \frac{1}{2} \sum_{i=1}^N \left(\int \frac{Z_1 |\phi_N(x)|^2}{|x_i + (R/2)\hat{n}|^2} dx + \int \frac{Z_2 |\phi_N(x)|^2}{|x_i - (R/2)\hat{n}|^2} dx \right). \end{aligned}$$

Using the uncertainty principle lemma (see for example [11], X2) we obtain

$$\begin{aligned} \frac{\partial e(R)}{\partial R} &\leq \frac{1}{2} \sum_{i=1}^N (4Z_1 \langle \phi_N | -\Delta_i | \phi_N \rangle + 4Z_2 \langle \phi_N | -\Delta_i | \phi_N \rangle) \\ &= 2(Z_1 + Z_2) \langle \phi_N | -\Delta | \phi_N \rangle \end{aligned}$$

that is

$$\langle \phi_N | -\Delta | \phi_N \rangle \geq \frac{1}{2(Z_1 + Z_2)} \frac{\partial e(R)}{\partial R}. \tag{10}$$

Using the virial theorem [12, 13] we can also write

$$\begin{aligned} \frac{\partial e(R)}{\partial R} &= \langle \phi_N | \frac{\partial V_R(x)}{\partial R} | \phi_N \rangle \\ &= \langle \phi_N | \frac{1}{R} (-V_R(x) - x \nabla V_R(x)) | \phi_N \rangle \end{aligned}$$

$$\begin{aligned}
 &= \frac{1}{R} \langle \phi_N | -V_R(x) + 2\Delta | \phi_N \rangle \\
 &= -\frac{1}{R} e(R) - \frac{1}{R} \langle \phi_N | -\Delta | \phi_N \rangle.
 \end{aligned} \tag{11}$$

From (10) and (11) it follows that

$$\frac{\partial e(R)}{\partial R} \leq -\frac{1}{R} e(R) - \frac{1}{2R(Z_1 + Z_2)} \frac{\partial e(R)}{\partial R}$$

and, therefore,

$$\frac{\partial}{\partial R} \left\{ \left(R + \frac{1}{2(Z_1 + Z_2)} \right) e(R) \right\} \leq 0.$$

Hence, $(R + 1/2(Z_1 + Z_2))e(R)$ is a non-increasing function of R , which, therefore, attains its maximum value at $R = 0$, i.e.

$$\left(R + \frac{1}{2(Z_1 + Z_2)} \right) e(R) \leq \frac{e(0)}{2(Z_1 + Z_2)} = \frac{E_{\text{at}}(N, Z_1 + Z_2)}{2(Z_1 + Z_2)}$$

which implies the lemma. \square

From this lemma we can obtain two direct results. The first result asserts that the electronic contribution converges to the energy of an atom when $R \rightarrow 0$. In fact, taking the limit on the lemma we obtain

$$e_N(Z_1, Z_2, 0^+) = E_N^{\text{at}}(Z_1 + Z_2). \tag{12}$$

The second result is an upper bound on the derivative of $e_N(Z_1, Z_2, R)$ in $R = 0^+$. From a direct calculation we obtain

$$\frac{1}{R} (e_N(Z_1, Z_2, R) - e_N(Z_1, Z_2, 0)) \leq \frac{1}{R} (1 - 2(Z_1 + Z_2)R + O(R^2) - 1) E_N^{\text{at}}(Z_1 + Z_2) \tag{13}$$

and, therefore,

$$\frac{\partial}{\partial R} e_N(Z_1, Z_2, R) |_{R=0^+} \leq -2(Z_1 + Z_2) E_N^{\text{at}}(Z_1 + Z_2). \tag{14}$$

3. Upper bounds on the kinetic energy

Proof of theorem 1 [14]. Using Bach's method [4] we can write

$$\begin{aligned}
 e_N(Z_1, Z_2, R) &= \langle \phi_N | \sum_{i=1}^N \left(-\Delta_i - \frac{Z_1}{|x_i + (R/2)\hat{n}|} - \frac{Z_2}{|x_i - (R/2)\hat{n}|} \right) \\
 &\quad + \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|} | \phi_N \rangle \\
 &\geq \frac{1}{2} \langle \phi_N | \sum_{i=1}^N -\Delta_i | \phi_N \rangle \\
 &\quad + \frac{Z_1}{2(Z_1 + Z_2)} \langle \phi_N | \sum_{i=1}^N \left(-\Delta_i - \frac{2(Z_1 + Z_2)}{|x_i + (R/2)\hat{n}|} \right) + \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|} | \phi_N \rangle \\
 &\quad + \frac{Z_2}{2(Z_1 + Z_2)} \langle \phi_N | \sum_{i=1}^N \left(-\Delta_i - \frac{2(Z_1 + Z_2)}{|x_i - (R/2)\hat{n}|} \right) + \sum_{1 \leq i < j \leq N} \frac{1}{|x_i - x_j|} | \phi_N \rangle
 \end{aligned}$$

$$\begin{aligned} &\geq \frac{1}{2} \langle \phi_N | \sum_{i=1}^N -\Delta_i | \phi_N \rangle + \frac{Z_1}{2(Z_1 + Z_2)} E_{\text{at}}(N, 2(Z_1 + Z_2)) \\ &\quad + \frac{Z_2}{2(Z_1 + Z_2)} E_{\text{at}}(N, 2(Z_1 + Z_2)) \\ &= \frac{1}{2} \langle \phi_N | \sum_{i=1}^N -\Delta_i | \phi_N \rangle + \frac{1}{2} E_{\text{at}}(N, 2(Z_1 + Z_2)) \end{aligned}$$

where we have used the variational characterization of $E_{\text{at}}(N, Z)$. From this last equation and lemma 1 we conclude

$$\langle \phi_N | \sum_{i=1}^N -\Delta_i | \phi_N \rangle \leq \frac{2}{(1 + 2(Z_1 + Z_2)R)} E_{\text{at}}(N, Z_1 + Z_2) - E_{\text{at}}(N, 2(Z_1 + Z_2)).$$

As in [6, 15], let us consider the function $\epsilon^N(\eta)$, with $\eta \geq 0$, which corresponds to the ground-state energy of the Hamiltonian

$$H^N(\eta) = \sum_{i=1}^N \left(-\Delta_i - \frac{1}{|x_i|} \right) + \sum_{1 \leq i < j \leq N} \frac{\eta}{|x_i - x_j|}.$$

It is well known [8] that $\epsilon^N(\eta)$ is monotone increasing, in particular $\epsilon^N(\eta) \geq \epsilon^N(0)$. Moreover, $\epsilon^N(\eta)$ is concave and

$$E_{\text{at}}(N, Z) = Z^2 \epsilon^N(1/Z).$$

Therefore,

$$\langle \phi_N | \sum_{i=1}^N -\Delta_i | \phi_N \rangle \leq \frac{2(Z_1 + Z_2)^2}{(1 + 2(Z_1 + Z_2)R)} \epsilon^N \left(\frac{1}{Z_1 + Z_2} \right) - 4(Z_1 + Z_2)^2 \epsilon^N \left(\frac{1}{2(Z_1 + Z_2)} \right). \tag{15}$$

Using the concavity and the monotonicity of $\epsilon^N(\eta)$ it follows from (15) that

$$\begin{aligned} \langle \phi_N | \sum_{i=1}^N -\Delta_i | \phi_N \rangle &\leq \frac{2(Z_1 + Z_2)^2}{(1 + 2(Z_1 + Z_2)R)} \epsilon^N \left(\frac{1}{Z_1 + Z_2} \right) - 2(Z_1 + Z_2)^2 \epsilon^N \left(\frac{1}{Z_1 + Z_2} \right) \\ &\quad - 2(Z_1 + Z_2)^2 \epsilon^N(0) \\ &= - \frac{4(Z_1 + Z_2)^2 R}{(1 + 2(Z_1 + Z_2)R)} \epsilon^N \left(\frac{1}{Z_1 + Z_2} \right) - 2(Z_1 + Z_2)^2 \epsilon^N(0) \\ &\leq - \frac{4(Z_1 + Z_2)^2 R}{(1 + 2(Z_1 + Z_2)R)} \epsilon^N(0) - 2(Z_1 + Z_2)^2 \epsilon^N(0) \\ &= 2(Z_1 + Z_2)^2 \left\{ \frac{1 + 4(Z_1 + Z_2)R}{1 + 2(Z_1 + Z_2)R} \right\} (-\epsilon^N(0)) \end{aligned}$$

which proves the theorem. □

To prove the second theorem we will need to use a result proved by Lieb and Simon in [3]:

Lemma 2. For all $R > 0$

$$\frac{\partial}{\partial R} e_1(Z_1, Z_2, R) \geq 0. \tag{16}$$

This lemma was proved by Hoffmann-Ostenhof [16]. A version valid for multi-centre one-electron systems was proved by Benguria in [17].

Proof of theorem 2 [14]. Taking equation (11) for all $R > 0$ and using lemma 2 we have

$$\langle \phi_1 | -\Delta | \phi_1 \rangle \leq -e(R) \quad (17)$$

where ϕ_1 is the ground state of the diatomic molecule with one electron and $e(R) = e_1(Z_1, Z_2, R)$. Therefore, we can use the united atom bound and obtain

$$\langle \phi_1 | -\Delta | \phi_1 \rangle \leq -E_1^{\text{at}}(Z_1 + Z_2) = \frac{1}{4}(Z_1 + Z_2)^2. \quad (18)$$

□

4. An upper bound on the electronic density at the nuclei

One of the problems that has attracted attention in mathematical physics in recent years has been the determination of upper bounds on the electronic density at the atomic nucleus. The first rigorous global result is the bound given by Hoffmann-Ostenhof and Hoffmann-Ostenhof [18]. For large atoms (i.e. $Z \rightarrow \infty$) the best result to date is the bound by Siedentop [20] who proved a conjecture argued by Narnhofer.

The density of the electrons at the nuclei of molecules or clusters in general appeared in a paper by Lieb and Thirring [21] as a parameter in the energy of the cluster. In their paper, Lieb and Thirring proved the universality of van der Waals forces for Coulomb systems. For diatomic molecules with one electron Hogreve [19] plotted this function numerically. In this section we will give a bound on the density of the electrons at the nuclei for diatomic molecules which depends on the distance of separation between the nuclei.

The electronic density is defined as

$$\rho(x) = \sum_{\sigma=\pm 1/2} \int_{[\mathbb{R}^3 \times \mathbb{C}^{2^{N-1}}]} |\phi_N(x, \sigma; x_2; \dots; x_N)|^2 dx_2 \dots dx_N \quad (19)$$

where the sums over the spin variables of the electrons x_2 to x_N are implicit in the integral.

The bound for the electronic density at the nucleus given in [18] can be extended to the case of diatomic molecules [21] to give

$$\rho(\text{nuclei}) \leq \frac{1}{3} \sum_{i=1}^N \langle \phi_N | \left\{ \frac{Z_1}{|x_i + (R/2)\hat{n}|^2} + \frac{Z_2}{|x_i - (R/2)\hat{n}|^2} \right\} | \phi_N \rangle \quad (20)$$

where ϕ_N is the ground state of the molecule.

As in [21] we can bound this expression from above using the uncertainty principle [11]:

$$\rho(\text{nuclei}) \leq \frac{1}{3} \sum_{i=1}^N (4Z_1 \langle \phi_N | -\Delta_i | \phi_N \rangle + 4Z_2 \langle \phi_N | -\Delta_i | \phi_N \rangle) = \frac{4}{3}(Z_1 + Z_2)K. \quad (21)$$

Therefore, we can use our bound on the kinetic energy, already proved, to obtain

$$\rho(\text{nuclei}) \leq \frac{1}{3}(Z_1 + Z_2)^3 \quad (22)$$

for molecules with $N = 1$, and

$$\rho(\text{nuclei}) \leq \frac{8}{3}(Z_1 + Z_2)^3 \left\{ \frac{1 + 4(Z_1 + Z_2)R}{1 + 2(Z_1 + Z_2)R} \right\} (-\epsilon^N(0)) \quad (23)$$

for $N > 1$.

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