Bounds on Diatomic Molecules in a Relativistic Model

Natalie Gilka

Department of Mathematical Sciences, University of Copenhagen,
Universitetsparken 5, 2100 Copenhagen Ø, Denmark

Abstract

We consider diatomic systems in which the kinetic energy of the electrons is treated in a simple relativistic model. The Born–Oppenheimer approximation is assumed. We investigate questions of stability, deducing bounds on the number $N$ of electrons, the binding energy $\Delta E_b$ and the equilibrium bond distance $R_0$. We use a known localization argument adopted to the present relativistic setting, with particular consideration of the critical point of stability, as well as the recently proved relativistic Scott correction.
I. INTRODUCTION

In this paper we study the stability of diatomic systems in the Born–Oppenheimer formulation. The kinetic energy of the electrons is treated in a model which accounts for relativistic effects. We employ a known localization argument applied by Solovej [1] to prove a lower bound on the number $N$ of electrons. This involves establishing an estimate of the equilibrium bond distance $R_0$ as a function of $N$ which requires particular consideration in the relativistic case due to the critical point of stability for large values of the nuclear charges. Bounds on the binding energy $\Delta E_b$ and on $R_0$ are deduced using the recently proved relativistic Scott correction [2].

We introduce positive numbers $Z_1, Z_2$, $Z = (Z_1, Z_2)$, which correspond in a physical picture to nuclear charges of a diatomic molecule, and denote the nuclear coordinates as $R_1, R_2 \in \mathbb{R}^3$. We consider furthermore a set of $N$ electrons and introduce the electron coordinates $x_i \in \mathbb{R}^3$, $i = 1, \ldots, N$. The coordinate origin is placed at $\frac{1}{2}(R_1 + R_2)$. Let $R_1 = R/2$, $R_2 = -R/2$, where $R = R_1 - R_2$, furthermore $R = |R_1 - R_2|$. We are working in units where $m = e = \hbar = 1$ ($m$: electron mass; $e$: electron charge; $\hbar$: Planck’s constant). In this unit system, the distance is measured in Bohr radii $a_0 = \hbar^2/mc^2$. The Hamiltonian employed in the present context is then

$$H(N, Z, R; \alpha) = \sum_{i=1}^{N} \left( \sqrt{-\alpha^{-2} \Delta_i} + \alpha^{-4} - \alpha^{-2} \right) - \sum_{i=1}^{N} \left( \frac{Z_1}{|x_i - R_1|} + \frac{Z_2}{|x_i - R_2|} \right) + \sum_{i<j} \frac{1}{|x_i - x_j|} + \frac{Z_1 Z_2}{R}$$

$$= H^\alpha + H_{en} + H_{ee} + H_{nn}. \quad (1)$$

$\alpha$ denotes the dimensionless fine-structure constant. It can be viewed as a quantifier of the relativistic correction and is in our unit system defined as $\alpha = c^{-1}$, where $c$ denotes the speed of light. In the nonrelativistic limit, we have $\alpha \to 0$. We assume the Born–Oppenheimer approximation, i.e., fixed nuclei positions $R_1, R_2$ corresponding to infinite nuclear masses $M_1 = M_2 = \infty$, and obtain therefore a parametrical dependence of the Hamiltonian on $R$.

The terms $H_{en}, H_{ee}, H_{nn}$ denote two-particle operators describing the classical Coulomb interaction between electrons ($e$) and nuclei ($n$). The term $H^\alpha$ in (1) is a one-particle
operator considering the kinetic energy of electrons of mass \( m \), with \( \Delta_i \) referring to the Laplacian of the \( i \)-th electron. This form of the operator represents the simplest model that attempts to include relativistic effects\(^3\). It does not give accurate numerical agreement with experimental observations, however, it does provide a qualitatively sensible description. For \( \alpha = 0 \) we retrieve the nonrelativistic limit of the kinetic energy of the \( i \)-th electron of \(-\frac{1}{2}\Delta_i\). The simple model chosen here has in common with all other relativistic approaches that it predicts instability of large atoms and molecules. The relevant parameter in this context is the product of the atomic numbers \( Z_k \), \( k = 1, 2 \), and the fine-structure constant \( \alpha \). The correct critical value of \( Z_k \alpha \) as derived from the study of the Dirac equation is expected to assume \( Z_k \alpha = 1 \). If the interest lies in the consideration of the limiting behaviour for \( Z_k \rightarrow \infty \), one is therefore required to bound \( Z_k \alpha \) by imposing \( \alpha \rightarrow 0 \), as was done in\(^2\). While this is from a physical perspective not sensible as the fine-structure constant exhibits an experimentally established value of approximately \( 1/137 \), it permits though a mathematical consideration of the asymptotics. The above discussion referred to the case of a diatomic system; the same is true for more complicated models.

Concerning the abovementioned relativistic instability quantitatively, we recognize that our simple relativistic model exhibits a known deficiency in that its point of instability is in contradiction with the expected value of \( Z_k \alpha = 1 \). In our model, the ground state energy \( E(N, Z, R; \alpha) \) is finite if \( \max \{Z_k \alpha\} \leq 2/\pi \), but \( E(N, Z, R; \alpha) = -\infty \) if \( \max \{Z_k \alpha\} > 2/\pi \) (see\(^6\),\(^8\), as well as\(^4\),\(^4\),\(^5\) for further discussion). This imposes that the atomic number has to be smaller than or equal to \( 2/\pi \alpha \approx 87 \), thereby contradicting the observation of atoms with atomic numbers larger than 87 to be stable. It is therefore clear that while our model is qualitatively reliable, we cannot expect good quantitative agreement.

The operator \( H(N, Z, R; \alpha) \) acts on the fermionic space \( \bigwedge^n L^2(\mathbb{R}^3; \mathbb{C}^2) \). The energy \( E(N, Z, R; \alpha) \) as a function of \( R \) is given as

\[
E(N, Z, R; \alpha) = \inf \text{ spec } H(N, Z, R; \alpha).
\]

We introduce the energy minimum (or rather infimum) of the molecule

\[
E(N, Z; \alpha) = \inf_R E(N, Z, R; \alpha).
\]
That $E(N, Z; \alpha) > -\infty$, i.e., the stability of relativistic molecules, was first proved by Daubechies and Lieb\[9\. A more general proof is due to Conlon\[7\] and Fefferman and de la Lave\[8\].

We say that the molecule has a stable Born–Oppenheimer ground state if the following two requirements are satisfied.

(1). 
$$E(N, Z; \alpha) < E(N, Z, R = \infty; \alpha) := \lim_{R \to \infty} E(N, Z, R; \alpha).$$

(2). The infimum is attained for some $R_0$, i.e.,
$$E(N, Z; \alpha) = E(N, Z, R_0; \alpha),$$

with the further requirement that it is an eigenvalue below the essential spectrum for $H(N, Z, R; \alpha)$ if $R = R_0$.

The first requirement ensures that the individual atoms stay bounded, the second requirement ensures that all electrons remain bounded to the molecule when the bond distance is $R_0$. We identify in the physical context $R_0$ as an equilibrium bond distance, i.e., the distance between $R_1, R_2$ in a stable molecule. Note that we do not exclude the existence of more than one $R_0$; this case plays no role in the present consideration though.

If stability holds, by which we mean the existence of a stable Born–Oppenheimer ground state as defined above, we introduce the binding energy for a molecule as

$$\Delta E_b(N, Z; \alpha) = E(N, Z, R = \infty; \alpha) - E(N, Z, R_0; \alpha) > 0.$$ (4)

We state first the main results of this paper before establishing the proofs in the subsequent sections. The final proofs of Theorem 1 and Theorem 2 can be found in Sec. V and Sec. VI respectively while Secs. II-IV introduce necessary prerequisites.

**Theorem 1** Assume $H(N, Z, R; \alpha)$ has a stable ground state for some $Z = Z_1 + Z_2$, with $\max_k \{Z_k \alpha\} < 2/\pi$. Let $\varepsilon > 0$ be such that $\max_k \{Z_k \alpha\} \leq \frac{2}{\pi}(1 - \varepsilon)$. Then, independent of particle symmetry,

$$\frac{Z_1Z_2}{Z_1+Z_2} \leq N \left( \frac{1}{2} + \sqrt{\frac{1}{4} + 3 \sigma(\varepsilon, \tau)} \right),$$

4
with \( \sigma(\varepsilon, \tau) = 2 \left[ 1 + \varepsilon^{-1} (1 - \varepsilon)^{-1} \right] \tau \), where \( \tau > 0 \) is the constant in Lemma 3, \((21)\).

Assuming fermions, we obtain instead

\[
\frac{Z_1 Z_2}{Z_1 + Z_2} \leq N \left( \frac{1}{2} + \sqrt{\frac{1}{4} + \frac{3\sigma(\varepsilon, \tau)}{N^{2/3}}} \right). \tag{6}
\]

A consideration of the case \( Z_1 \gg Z_2 \) shows that the bound on \( N \) is actually controlled by the smaller of the two atoms.

An upper bound on \( N \) is given by Lieb\([10]\) as \( N < 2(Z_1 + Z_2) + 2 \), valid for the nonrelativistic as well as the relativistic case. In the latter, Dall’Acqua, Sørensen and Stockmeyer\([11]\) proved this bound to hold for \( \max_k \{Z_k \alpha\} < 2/\pi \).

**Theorem 2**  There exist constants \( c_1, c_2 > 0 \) such that if \( H(N, Z, R; \alpha) \) has a stable ground state on the fermionic space for \( Z = Z_1 + Z_2, Z = N, \max_k \{Z_k \alpha\} < 2/\pi, k = 1, 2 \), then

\[
0 < \Delta E_b(Z; \alpha) < c_1 Z^{2-1/30} \tag{7}
\]

\[
R_0 \geq c_2 Z^{-1/3+11/210}. \tag{8}
\]

From Thomas–Fermi theory we know that the bulk of electrons around one nucleus is at a distance \( Z^{-1/3} \) from that nucleus. Thus the theorem states that the internuclear distance is much larger than the radius of the bulk electron cloud.

The approach in the proof of Theorem 1 consists of the introduction of localization functions \( \chi_1, \chi_2 \in H^1(\mathbb{R}^3 \times \mathbb{R}^3) \) satisfying

\[
\chi_1(x, R)^2 + \chi_2(x, R)^2 = 1. \tag{9}
\]

The nonrelativistic terms \( H_{ee} + H_{en} + H_{nn} \) can be treated according to a localization argument following [1]. The nonlocal operator \( H^a \) will be treated separately, applying here results from [2]. We will begin with this consideration in Sec. [II] before introducing
the localization argument in Sec. III. In Sec. IV we establish an estimate on $R_0$ as a function of $N$. We introduce in this context Lemma 3 and Theorem 4, the proofs of which can be found in the appendix. These results will be used in Sec. V to prove Theorem 1, i.e., to derive a global bound on $N$. Theorem 2 will be proved in Sec. VI, where we will apply the recently proved relativistic Scott correction\cite{2} to derive bounds on $\Delta E_b, R_0$.

We will in the following denote the wave function of the many-particle system by $\Psi$, with $\Psi \in \bigwedge^N L^2(\mathbb{R}^3 \times \{-1, +1\})$, and $\|\Psi\|^2_2 = 1$.

II. RELATIVISTIC IMS FORMULA

We will first consider the kinetic energy operator $H^\alpha = \sum_i T^\alpha_i$ separately by application of the relativistic Ismagilov–Morgan–Simon (IMS) formula. This formula was proved in \cite{2} generally for a family $(\xi_u)_{u \in \mathcal{M}}$ of positive bounded $C^1$-functions on $\mathbb{R}^3$ with bounded derivatives which, given a positive measure $d\mu$ on $\mathcal{M}$, fulfill $\int_{\mathcal{M}} \xi_u(x)^2 d\mu(u) = 1$ for all $x \in \mathbb{R}^3$. We consider in the present context the set of two localization functions $\chi_1, \chi_2$. The formula reduces in this case, for any $\psi \in H^{1/2}(\mathbb{R}^3)$, to

\[
\langle \psi | \left( \sqrt{-\alpha^{-2} \Delta + \alpha^{-4} - \alpha^{-2}} \right) | \psi \rangle = \langle \psi | T^\alpha | \psi \rangle = \langle \psi | \chi_1 T^\alpha \chi_1 | \psi \rangle - \langle \psi | L_{\chi_1} | \psi \rangle + \langle \psi | \chi_2 T^\alpha \chi_2 | \psi \rangle - \langle \psi | L_{\chi_2} | \psi \rangle,
\]

with $L_{\chi_k}$ denoting an operator with integral kernel

\[
L_{\chi_k}(x,y) = (2\pi)^{-2} \alpha^{-3} |x - y|^{-2} K_2 \left( \alpha^{-1} |x - y| \right) \left[ \chi_k(x) - \chi_k(y) \right]^2,
\]

where $K_2$ is a modified Bessel function defined by

\[
K_2(t) = t \int_0^\infty e^{-t\sqrt{s^2+1}} s^2 ds.
\]

Note that our choice of unit system differs from \cite{2}, Theorem 13 (Relativistic IMS formula), in setting $m = 1$. 

Employing the relativistic IMS formula, we can reformulate the following matrix element as

$$\langle \Psi | H^\alpha | \Psi \rangle = \sum_i \left\{ \langle \Psi | \chi_1 T^\alpha_i \chi_1 | \Psi \rangle + \langle \Psi | \chi_2 T^\alpha_i \chi_2 | \Psi \rangle - \langle \Psi | L_{\chi_1}(x_i, y_i) | \Psi \rangle - \langle \Psi | L_{\chi_2}(x_i, y_i) | \Psi \rangle \right\}. \quad (13)$$

III. LOCALIZATION ARGUMENT

We consider now two-cluster decompositions \( \theta = (\theta_1, \theta_2) \) of \( \{1, \ldots, N\} \). The interactions within the two separate clusters are described by \( H_{\theta_1}, H_{\theta_2} \), with \( H_\theta = H_{\theta_1} + H_{\theta_2} \) and

$$H_{\theta_k} = \sum_{i \in \theta_k} \left( \sqrt{-\alpha^{-2} \Delta_i + \alpha^{-4}} - \alpha^{-2} \right) - \sum_{i \in \theta_k} \frac{Z_k}{|x_i - R_k|} + \sum_{i < j} \frac{1}{|x_i - x_j|}, \quad (14)$$

while the intercluster potential \( I_\theta \) can be given as

$$I_\theta = -\sum_{i \in \theta_2} \frac{Z_1}{|x_i - R_1|} - \sum_{i \in \theta_1} \frac{Z_2}{|x_i - R_2|} + \sum_{i \in \theta_1, j \in \theta_2} \frac{1}{|x_i - x_j|} + \frac{Z_1 Z_2}{R}, \quad (15)$$

and we recognize that \( H = H_\theta + I_\theta \).

The space of localization functions can be correspondingly regrouped as

$$\prod_{i=1}^{N} \left( \chi_1(x_i)^2 + \chi_2(x_i)^2 \right) = \sum_{\theta} \prod_{i \in \theta_1} \chi_1(x_i)^2 \prod_{j \in \theta_2} \chi_2(x_j)^2 = \sum_{\theta} \chi_\theta^2$$

with \( \chi_\theta = \prod_{i \in \theta_1} \chi_1(x_i) \prod_{j \in \theta_2} \chi_2(x_j) \), omitting here and from now on out of reasons of simplicity the dependence in \( R \).

We consider, starting from (13), that

$$\langle \Psi | H^\alpha | \Psi \rangle = \sum_i \left\{ \langle \Psi | \chi_1 T^\alpha_i \chi_1 | \Psi \rangle \prod_{j \neq i}^{N} \left( \chi_1(x_j)^2 + \chi_2(x_j)^2 \right) | \Psi \rangle 
+ \langle \Psi | \chi_2 T^\alpha_i \chi_2 | \Psi \rangle \prod_{j \neq i}^{N} \left( \chi_1(x_j)^2 + \chi_2(x_j)^2 \right) | \Psi \rangle \right\}$$

$$- \sum_i \left\{ \langle \Psi | L_{\chi_1}(x_i, y_i) | \Psi \rangle + \langle \Psi | L_{\chi_2}(x_i, y_i) | \Psi \rangle \right\}$$

$$= \sum_\theta \left\{ \langle \Psi | \chi_\theta \sum_i T^\alpha_i \chi_\theta | \Psi \rangle \right\}$$

$$- \sum_i \left\{ \langle \Psi | L_{\chi_1}(x_i, y_i) | \Psi \rangle + \langle \Psi | L_{\chi_2}(x_i, y_i) | \Psi \rangle \right\}. \quad (13)$$
and furthermore reformulate the Coulomb terms straightforwardly
\[
\langle \Psi | (H - H^\alpha) | \Psi \rangle = \sum_\theta \langle \Psi | (H - H^\alpha) \chi_\theta^2 | \Psi \rangle = \sum_\theta \langle \Psi | \chi_\theta (H - H^\alpha) \chi_\theta | \Psi \rangle.
\]

Additionally, we recall that if \( H \) has a stable ground state then
\[
E(N, Z; \alpha) = \inf \text{ spec } H(N, Z, R; \alpha)|_{R=R_0} < E_\theta(N, Z, R_0; \alpha)
= \inf \text{ spec } H_\theta(N, Z, R; \alpha)|_{R=R_0}.
\]
This is the Hunziker–van Winter–Zhislin (HVZ) theorem[12], in its formulation for this operator.

We can therefore estimate
\[
R\langle \Psi | H | \Psi \rangle = R \sum_\theta \left\{ \langle \Psi | \chi_\theta H^\alpha \chi_\theta | \Psi \rangle + \langle \Psi | \chi_\theta (H - H^\alpha) \chi_\theta | \Psi \rangle \right\}
- R \sum_i \left\{ \langle \Psi | L_{\chi_1}(x_i, y_i) | \Psi \rangle + \langle \Psi | L_{\chi_2}(x_i, y_i) | \Psi \rangle \right\}
= R \sum_\theta \left\{ \langle \Psi | \chi_\theta H_\theta \chi_\theta | \Psi \rangle + R \langle \Psi | I_{\theta} \chi_\theta^2 | \Psi \rangle \right\}
- R \sum_i \left\{ \langle \Psi | L_{\chi_1}(x_i, y_i) | \Psi \rangle + \langle \Psi | L_{\chi_2}(x_i, y_i) | \Psi \rangle \right\}
\geq R_0 \sum_\theta \left\{ E_\theta \langle \Psi | \chi_\theta^2 | \Psi \rangle + \langle \Psi | I_{\theta} \chi_\theta^2 | \Psi \rangle \right\}
- R_0 \sum_i \left\{ \langle \Psi | L_{\chi_1}(x_i, y_i) | \Psi \rangle + \langle \Psi | L_{\chi_2}(x_i, y_i) | \Psi \rangle \right\}
\geq R_0 \inf_\theta E_\theta + R_0 \sum_\theta \langle \Psi | I_{\theta} \chi_\theta^2 | \Psi \rangle
- R_0 \sum_i \left\{ \langle \Psi | L_{\chi_1}(x_i, y_i) | \Psi \rangle + \langle \Psi | L_{\chi_2}(x_i, y_i) | \Psi \rangle \right\}.
\]
We obtain a bound on the localization error \( \langle \psi | L_{\chi_k}(x, y) | \psi \rangle \) in the following as
\[
|\langle \psi | L_{\chi_k}(x, y) | \psi \rangle| \leq (2\pi)^{-\alpha - 3} \int |\psi(x)||\psi(y)| K_2 \left( \alpha^{-1} |x - y| \right) \frac{|\chi_k(x) - \chi_k(y)|^2}{|x - y|^2} \, dx \, dy \\
\leq (2\pi)^{-\alpha - 3} \| \nabla \chi_k \|_\infty^2 \int |\psi(x)||\psi(y)| K_2 \left( \alpha^{-1} |x - y| \right) \, dx \, dy \\
\leq (2\pi)^{-\alpha - 3} \| \nabla \chi_k \|_\infty^2 \int |\psi(x)|^2 K_2 \left( \alpha^{-1} |x - y| \right) \, dx \, dy \\
= (2\pi)^{-\alpha - 2} \| \nabla \chi_k \|_\infty^2 \int |\psi(x)|^2 \int K_2 \left( |y| \right) \, dy \\
= \frac{3}{2} \| \nabla \chi_k \|_\infty^2 \| \psi \|_2^2,
\] (17)
where in the third step we used the Cauchy-Schwarz inequality and \( K_2 \geq 0 \). We obtain from this the final estimate
\[
- \Delta E_b(N, Z; \alpha) R_0 \geq - \frac{3}{2} N R_0 \left\{ \| \nabla \chi_1 \|_\infty^2 + \| \nabla \chi_2 \|_\infty^2 \right\} \\
- R_0 \sum_{i=1}^N \langle \Psi | \frac{Z_1}{|x_i - R_1|} \chi_2(x_i)^2 + \frac{Z_2}{|x_i - R_2|} \chi_1(x_i)^2 | \Psi \rangle \\
+ R_0 \sum_{i<j}^N \langle \Psi | \frac{1}{|x_i - x_j|} \left( \chi_1(x_i)^2 \chi_2(x_j)^2 + \chi_1(x_j)^2 \chi_2(x_i)^2 \right) | \Psi \rangle \\
+ Z_1 Z_2.
\] (18)

IV. ESTIMATE ON \( R_0 \)

Following [1] we introduce explicit expressions for the localization functions which exhibit a dependence on the parameter \( \mu = Z_2/Z_1 \). We impose for convenience \( Z_1 \geq Z_2 \), therefore \( \mu \leq 1 \). Introducing
\[
\overline{x} = x + \frac{1 - \mu}{2(\mu + 1)} (R_1 - R_2) \quad \text{and} \quad \overline{R} = \frac{1}{\mu + 1} (R_1 - R_2)
\]
we obtain
\[
\overline{x} + \mu \overline{R} = x - R_2 \quad \text{and} \quad \overline{x} - \overline{R} = x - R_1,
\]
using that \( R_2 = -R_1 \).
We define the localizing functions as

\[
\chi_1(x) = \frac{|x + \mu \mathbf{R}|}{\sqrt{\mu + 1}(|x|^2 + \mu R^2)^{1/2}}
\]

\[
\chi_2(x) = \frac{\sqrt{\mu} |x - \mathbf{R}|}{\sqrt{\mu + 1}(|x|^2 + \mu R^2)^{1/2}},
\]

with \( \mathbf{R} = |\mathbf{R}|. \) It is straightforward to see that

\[
\chi_1(x)^2 + \chi_2(x)^2 = 1.
\]

We evaluate

\[
R \left( (\nabla \chi_1(x))^2 + (\nabla \chi_2(x))^2 \right) = \frac{\mu}{(\mu + 1)^2} \left( |x|^2 + \mu R^2 \right)^2 \leq \frac{(\mu + 1)^2}{\mu} R^{-1}.
\]

We will use this expression for \( R \) being the equilibrium bond distance \( R_0 \). We recognize that an estimate on \( R_0^{-1} \) is necessary to subsequently deduce an estimate on the localization error. Obtaining this estimate is more involved in the relativistic case than in the nonrelativistic one due to the presence of the critical point if \( Z_k \alpha = \frac{\pi}{2} \) for some \( k \). We start out by comparing the energy \( E \) of the diatomic system with the situation of localizing all electrons on one of the centers, say \( \mathbf{R}_1 \). We obtain using the stability conditions (2), (3) that for the energy \( E^{at} \) of a single atom

\[
E^{at}(N, Z_1; \alpha) \geq \lim_{R \to \infty} E(N, \mathbf{Z}, R; \alpha) \geq E(N, \mathbf{Z}, R_0; \alpha) \geq E^{at}(N, Z_1 + Z_2; \alpha) + \frac{Z_1 Z_2}{R_0}.
\]

The last inequality, the lower bound on the energy of a united atom, is simple to derive for the nonrelativistic case, as was done in [13] (Sec. (4.6.14)). The extension to the present case of the relativistic operator is straightforward as the form of the one-particle operator \( H^\alpha \) is identical for the molecular case and the united atom.

Establishing an upper bound on \( E^{at}(N, Z_1; \alpha) - E^{at}(N, Z_1 + Z_2; \alpha) \) will allow us to deduce an upper bound on \( R_0^{-1} \).
Since $Z \mapsto E^{at}(N, Z; \alpha)$ is a nonincreasing, concave function we have

$$\frac{E^{at}(N, Z; \alpha) - E^{at}(N, Z_1 + Z_2; \alpha)}{Z_2} \geq \left[ \frac{\partial E^{at}(N, Z_1 + Z_2; \alpha)}{\partial Z} \right]_-, $$

where $\left[ \frac{\partial}{\partial Z} \right]_-$ refers to the left derivative.

We note that if

$$\left[ \frac{\partial E^{at}(N, Z; \alpha)}{\partial Z} \right]_- = 0$$

we trivially have a lower bound of zero while if

$$\left[ \frac{\partial E^{at}(N, Z; \alpha)}{\partial Z} \right]_- < 0,$$

then $E^{at}(N, Z; \alpha) < 0$. In this case there is an $1 \leq n \leq N$ such that $E^{at}(N, Z; \alpha) = E^{at}(n, Z; \alpha) < E^{at}(n - 1, Z; \alpha)$ and there is an $n$-particle wave function $\Psi_n$ such that

$$H^{at}(n, Z; \alpha) \Psi_n = E^{at}(n, Z; \alpha) \Psi_n,$$

with $H^{at}(n, Z; \alpha)$ being the Hamiltonian of the atomic system.

By the Feynman-Hellman Theorem we have

$$\left[ \frac{\partial E^{at}(N, Z; \alpha)}{\partial Z} \right]_- \geq - \left( \Psi_n, \sum_{i=1}^n \frac{1}{|x_i|} \Psi_n \right),$$

and have therefore reformulated the problem into establishing an upper bound on

$$\left( \Psi_n, \sum_{i=1}^n \frac{1}{|x_i|} \Psi_n \right)$$

when $E^{at}(n, Z; \alpha) < 0$.

This we will achieve in the following by first providing a lower bound on

$$\sum_{i=1}^n \left[ \sqrt{-\alpha^2 \Delta_i + \alpha^{-4} - \alpha^{-2} - \frac{Z}{|x_i|}} \right] = \sum_{i=1}^n \left[ T_i^{\alpha} - \frac{Z}{|x_i|} \right]$$

for $Z \alpha \leq \frac{2}{\pi}$ (Lemma 3, (21)), which will be accomplished by use of the combined Daubechies–Lieb–Yau (DLY) inequality (see [2], furthermore [5, 14] for Daubechies inequality and Lieb–Yau inequality). This lower bound will then be used in the proof of Theorem 4, namely the upper bound on

$$\left( \Psi_n, \sum_{i=1}^n \frac{1}{|x_i|} \Psi_n \right),$$

for the case of $Z \alpha \leq \frac{2}{\pi} (1 - \varepsilon)$. After having established Theorem 4, we are in the position to return to (20) and provide a bound on
$R_0^{-1}$. We recognize that our approach fails for the critical case of $Z\alpha = \frac{2}{\pi}$.

**Lemma 3** If $Z\alpha \leq \frac{2}{\pi}$ then for all $n \geq 1$

$$\sum_{i=1}^{n} \left[ T_i^\alpha - \frac{Z}{|x_i|} \right] \geq -Z^2 \tau \begin{cases} n & \text{without particle symmetry} \\ n^{1/3} & \text{assuming fermions} \end{cases} = -Z^2 \kappa(n), \quad (21)$$

for some constant $\tau > 0$, with the function $\kappa(n)$ defined by (21).

**Theorem 4** Assume $Z\alpha \leq \frac{2}{\pi} (1 - \varepsilon)$, $0 < \varepsilon < 1$. Assume $\Psi_n$ eigenfunction of $H^{at}(n, Z; \alpha)$ with eigenvalue $E^{at}(n, Z; \alpha)$, where $1 \leq n \leq N$ and $E^{at}(N, Z; \alpha) = E^{at}(n, Z; \alpha) < E^{at}(n - 1, Z; \alpha)$. Then

$$\left[ \frac{\partial E^{at}(N, Z; \alpha)}{\partial Z} \right] \geq - \left( \Psi_n, \sum_{i=1}^{n} \frac{1}{|x_i|} \Psi_n \right) \geq - \left[ 1 + \varepsilon^{-1} (1 - \varepsilon)^{-1} \right] \kappa(n) Z. \quad (22)$$

The proofs of Lemma 3 and Theorem 4 can be found in the appendix.

We are now in the position to obtain our final estimate on $R_0^{-1}$. Starting with the bound on the united atom we reformulate

$$\frac{Z_1 Z_2}{R_0} \leq E^{at}(N, Z_1; \alpha) - E^{at}(N, Z_1 + Z_2; \alpha) \leq -Z_2 \left[ \frac{\partial E^{at}(N, Z_1 + Z_2; \alpha)}{\partial Z} \right] \leq Z_2 (Z_1 + Z_2) \left[ 1 + \varepsilon^{-1} (1 - \varepsilon)^{-1} \right] \kappa(N) \leq 2 \left[ 1 + \varepsilon^{-1} (1 - \varepsilon)^{-1} \right] \kappa(N) Z_1 Z_2,$$

with $Z_2 \leq Z_1$. We have used that $n \leq N$.

We therefore obtain

$$R_0^{-1} \leq \sigma(\varepsilon, \tau) \begin{cases} N & \text{without particle symmetry} \\ N^{1/3} & \text{assuming fermions} \end{cases} \quad (23)$$

where $\sigma(\varepsilon, \tau) = 2 \left[ 1 + \varepsilon^{-1} (1 - \varepsilon)^{-1} \right] \tau$, for some constants $1 > \varepsilon > 0$, $\tau > 0$, with $\tau$ introduced in Lemma 3, (21).
V. GLOBAL BOUND ON $N$

The estimate on $R_0$ as a function of $N$ allows us to estimate the localization error from (17) as

$$R_0 |\langle \psi | L_{x_1} (x,y) | \psi \rangle| + R_0 |\langle \psi | L_{x_2} (x,y) | \psi \rangle| \leq \frac{3}{2} R_0 \left\{ \| \nabla \chi_1 \|_\infty^2 + \| \nabla \chi_2 \|_\infty^2 \right\}$$

$$\leq 3 R_0 \left\| (\nabla \chi_1)^2 + (\nabla \chi_2)^2 \right\|_\infty$$

$$\leq 3 \sigma(\varepsilon, \tau) N \frac{(\mu + 1)^2}{\mu}.$$  \hfill (24)

Inspecting the remaining terms in (18), we recognize the difficulty in obtaining an estimate on the repulsion of electrons between different clusters and will neglect the term at this point. We thereby obtain from (18)

$$0 \geq -3 \sigma(\varepsilon, \tau) \frac{(\mu + 1)^2}{\mu} N^2 - R_0 \sum_{i=1}^{2N} \Psi \frac{Z_2 |\mathbf{x}_i + \mu \mathbf{R}| + \mu Z_1 |\mathbf{x}_i - \mathbf{R}|}{(\mu + 1)(|\mathbf{x}_i|^2 + \mathbf{R}^2)} |\Psi| + Z_1 Z_2.$$ \hfill (25)

We estimate following [1]

$$\left( Z_2 |\mathbf{x} + \mu \mathbf{R}| + \mu Z_1 |\mathbf{x} - \mathbf{R}| \right)^2 \leq (Z_1^2 + Z_2^2 \mu) \left( |\mathbf{x} + \mu \mathbf{R}|^2 + |\mathbf{x} - \mathbf{R}|^2 \right)$$

$$= (Z_1^2 + Z_2^2 \mu)(\mu + 1)(|\mathbf{x}|^2 + \mu \mathbf{R}^2)$$  \hfill (26)

and obtain with $\mu = Z_2/Z_1$

$$0 \geq -3 \sigma(\varepsilon, \tau) N^2 - N \frac{Z_1 Z_2}{Z_1 + Z_2} + \left( \frac{Z_1 Z_2}{Z_1 + Z_2} \right)^2,$$

therefore

$$\frac{Z_1 Z_2}{Z_1 + Z_2} \leq N \left( \frac{1}{2} + \sqrt{\frac{1}{4} + 3 \sigma(\varepsilon, \tau)} \right).$$

We compare this result to the nonrelativistic case where Solovej [1] proved

$$\frac{Z_1 Z_2}{Z_1 + Z_2} \leq N (3/2).$$

The difference in the bound on $N$ is attributable to the prefactor in the first term of (25) which is in the nonrelativistic case $-\frac{3}{4}$ instead of $-3\sigma(\varepsilon, \tau)$. Aside of the more demanding assessment of $R_0^{-1}$, which in the nonrelativistic case yields an estimate of $R_0^{-1} \leq \frac{3}{2} N$, we recognize two further steps in the present derivation which influence our bound. The simple estimate of $\| \nabla \chi_1 \|_\infty^2 + \| \nabla \chi_2 \|_\infty^2 \leq 2 \| (\nabla \chi_1)^2 + (\nabla \chi_2)^2 \|_\infty$ in the second step of (24)
introduces a factor of two. A further factor of three has to be attributed to the estimates in \[17\]. In particular, we bound the expression \(|\chi_k(x) - \chi_k(y)|\) by
\[
|\chi_k(x) - \chi_k(y)| \leq \| \nabla \chi_k \|_{\infty} \cdot |x - y|
\]
before employing subsequently the Cauchy-Schwarz inequality. Instead, it would be preferable to construct explicit forms for \(\chi_1, \chi_2\) which would allow a tighter estimate of \(\langle \psi | \mathcal{L} \chi_k | \psi \rangle\) while at the same time permitting an advantageous evaluation of the electron–nuclear attraction term in \(26\). With respect to the localization error, one has in particular to construct a form of localization functions which results in a cancellation of the denominator \(|x - y|\) in order to obtain a bound of \(\| \langle \psi | \mathcal{L} \chi_k | \psi \rangle \| < \infty\).

In the present context, we have decided to employ the particular forms of \(\chi_1, \chi_2\) given in \[1\] which result in an algebraically simple expression of the bound on \(N\) and recognize the scope that exists in the possible improvement on the bound of the localization error.

Considering alternatively the fermionic bound on \(R_0^{-1}\) in our estimate, we obtain
\[
\frac{Z_1Z_2}{Z_1 + Z_2} \leq N \left( \frac{1}{2} + \sqrt{\frac{1}{4} + \frac{3\sigma(\varepsilon, \tau)}{N^{2/3}}} \right).
\]
This can be compared to Benguria, Siedentop and Stockmeyer \[15\] who find a very similar expression for the case of homonuclear relativistic molecular ions. Their proof holds for \(Z \alpha \leq 1/2\), where \(Z = Z_1 + Z_2 = 2Z_1\).

**VI. BOUND ON \(\Delta E_0, R_0\)**

The first rigorous investigation of the limit \(Z_k \to \infty\) with \(Z_k \alpha\) bounded was given by Sørensen \[16\]. The leading asymptotics of the ground state were established to be determined by Thomas–Fermi theory. The first correction term, the Scott correction, and its dependence on \(Z_k \alpha\), was proved by Solovej, Sørensen and Spitzer \[2\] for a neutral molecular system, i.e., \(N = Z = \sum_1^M Z_k\), in the framework of the Born-Oppenheimer formulation.

We state their main theorem, the relativistic Scott correction, for the case of a diatomic system. Let \(Z = Z_1 + Z_2\), \(z = (z_1, z_2) = Z^{-1}Z\) with \(z_1, z_2 > 0\), whereby \(z_1 + z_2 = 1\). We define \(r = Z^{1/3}R,\) with \(|r| > r_0\) for some \(r_0 > 0\). Note that \(r = r_1 - r_2,\) with \(r_1, r_2 \in \mathbb{R}^3, \)
furthermore \( r = |\mathbf{r}_1 - \mathbf{r}_2| \). Then there exist a value \( E_{TF}(z, r) \) and a universal (independent of \( z \) and \( r \)) continuous, nonincreasing function \( S : [0, 2/\pi] \to \mathbb{R} \) with \( S(0) = 1/4 \) such that as \( Z \to \infty \) and \( \alpha \to 0 \), with \( \max_k \{ Z_k \alpha \} \leq 2/\pi \), we have

\[
E(Z, R; \alpha) = Z^{7/3} E_{TF}(z, r) + 2 Z_1 S(Z_1 \alpha) + 2 Z_2 S(Z_2 \alpha) + O(Z^{2-1/30}). \tag{27}
\]

The error term means that \( |O(Z^{2-1/30})| < c Z^{2-1/30} \), where the constant \( c \) only depends on \( r_0 \). Moreover, the Thomas–Fermi energy satisfies the scaling relation

\[
E_{TF}(Z, R) = Z^{7/3} E_{TF}(z, r). \tag{28}
\]

We introduce furthermore the estimate on the split of a diatomic system in Thomas–Fermi theory which was derived in [1] based on Brezis–Lieb [18]

\[
E_{TF}(z, r) \geq E_{TF}(z_1) + E_{TF}(z_2) + c r^{-7}, \tag{29}
\]

with some constant \( c \). \( E_{TF}(z_n) \) denotes the scaled Thomas–Fermi energy of a nucleus of charge \( n \) at the origin.

We consider now the case of a diatomic molecule and obtain by application of the relativistic
Scott correction (27) and furthermore (28), (29) that

\[ H(N, Z, R; \alpha) \geq E(Z, R; \alpha) \]

\[ \geq Z^{7/3} E^{TF}(z_1) + 2 Z_1^2 S(Z_1 \alpha) + Z^{7/3} E^{TF}(z_2) + 2 Z_2^2 S(Z_2 \alpha) \]

\[ + c_1 r^{-7} Z^{7/3} - c_0 Z^{2-1/30} \]

\[ = E^{TF}(Z z_1) + 2 Z_1^2 S(Z_1 \alpha) + E^{TF}(Z z_2) + 2 Z_2^2 S(Z_2 \alpha) \]

\[ + c_1 r^{-7} Z^{7/3} - c_0 Z^{2-1/30} \]

\[ = Z_1^{7/3} E^{TF}(1) + 2 Z_1^2 S(Z_1 \alpha) + Z_2^{7/3} E^{TF}(1) + 2 Z_2^2 S(Z_2 \alpha) \]

\[ + c_1 r^{-7} Z^{7/3} - c_0 Z^{2-1/30} \]

\[ \geq E(Z_1; \alpha) + E(Z_2; \alpha) + c_1 r^{-7} Z^{7/3} - c_0 Z^{2-1/30}, \]

with constants \(c_0, c_1\) (note that the definition of \(c_0\) changes in the last step).

We conclude

\[ E(N, Z, R; \alpha) - E(Z_1; \alpha) - E(Z_2; \alpha) \geq c_1 R_0^{-7} - c_0 Z^{2-1/30}, \]

and can therefore estimate

\[ 0 \geq c_1 R_0^{-7} - c_0 Z^{2-1/30} \]

\[ R_0 \geq c Z^{-1/3+11/210} \]

The constant \(c\) is independent of \(Z\) and \(R\) and may assume different values in different inequalities.

We compare to the nonrelativistic case where Solovej\[1]\ proved

\[ R_0 > c Z^{-(1/3)(1-\varepsilon)}, \]

for \(N \leq Z\) and \(\varepsilon = 1/70\).

We note that the reason for our bound to be better than the bound of Solovej is that we used that the energy is known up to the Scott correction. The same can be done in the nonrelativistic case and would give a similar bound. The nonrelativistic Scott correction
was proved by Ivrii and Sigal \cite{19} after the publication of \cite{1}.

Benguria, Siedentop and Stockmeyer \cite{15} state for homonuclear relativistic molecular ions a bound on $R_0$ (for $Z\alpha < 1/2$) which, translated into our unit system, corresponds to an error of the order $Z^{-1}$. The difference to our estimate reflects their consideration of boltzonic electrons.

Recalling that in the case of a stable ground state

$$\Delta E_b(N, Z; \alpha) < E(Z_1; \alpha) + E(Z_2; \alpha) - E(N, Z, R; \alpha),$$

we deduce furthermore a bound on $\Delta E_b(N, Z; \alpha)$ of

$$\Delta E_b(N, Z; \alpha) < c Z^{2^{-1/30}}. \quad (33)$$

VII. ACKNOWLEDGEMENT

I would like to thank Jan Philip Solovej for providing the framework for this work as well as for numerous insightful and stimulating discussions.

This work was supported by a fellowship within the Postdoc–Program of the German Academic Exchange Service (DAAD).

Appendix A: Proofs

1. Proof of Lemma 3

We begin with a separation of the nucleus–electron attraction by considering a ball $|x| < r$ for some $r$ to be chosen later. The contribution from the outside region is estimated by $-Z/r$. We assume $n \geq 1$.

$$\sum_{i=1}^{n} \left[ T_i^\alpha - \frac{Z}{|x_i|} \right] \geq \sum_{i=1}^{n} \left[ T_i^\alpha - \frac{Z}{|x_i|} 1_{\{|x_i| < r\}} \right] \geq \frac{nZ}{r}, \quad (A1)$$

where $1_{\{|x| < r\}}$ is the characteristic function of the ball $\{|x| < r\}$. 

17
A lower bound on the right-hand side is in the fermionic case obtained through a sum over all negative eigenvalues. In the case of no particle symmetry, a lower bound is obtained by approximating the bosonic states through \( n \) times the lowest eigenvalue, which is then in turn estimated by the sum of all negative eigenvalues.

\[
\sum_{i=1}^{n} \left[ T_{i}^{\alpha} - \frac{Z}{|x_i|} 1_{\{|x_i|<r\}} \right] - \frac{nZ}{r} \geq 2 \text{Tr} \left[ T^{\alpha} - \frac{Z}{|x|} 1_{\{|x|<r\}} \right] - \frac{nZ}{r} \quad \text{for spin 1/2 fermions} \quad (A2)
\]

\[
\sum_{i=1}^{n} \left[ T_{i}^{\alpha} - \frac{Z}{|x_i|} 1_{\{|x_i|<r\}} \right] - \frac{nZ}{r} \geq n \text{Tr} \left[ T^{\alpha} - \frac{Z}{|x|} 1_{\{|x|<r\}} \right] - \frac{nZ}{r} \quad \text{without symmetry} \quad (A3)
\]

We will use the combined Daubechies–Lieb–Yau inequality [2, 5, 14] to finalize the proof of Lemma 3. Note again that our form differs from [2], Theorem 16 (Combined Daubechies–Lieb–Yau inequality), in setting \( m = 1 \).

We state the combined DLY inequality in its application to the simpler case of a single atom. Assume a function \( W \in L_{1,\text{loc}}^{1}(\mathbb{R}^3) \) which satisfies

\[
W(x) \geq -\frac{\nu}{|x|} - C\nu\alpha^{-1} \quad \text{when} \quad |x| < \alpha, \quad (A4)
\]

with \( \alpha \nu \leq 2/\pi \), \( \alpha \geq 0 \), and a constant \( C \). Then

\[
\text{Tr} \left[ T^{\alpha} + W(x) \right] \geq -C\nu^{5/2}\alpha^{1/2} - C \int_{\alpha<|x|} |W(x)|^{5/2} dx \]

\[
-C\alpha^{3} \int_{\alpha<|x|} |W(x)|^{4} dx, \quad (A5)
\]

where, as above, \( T^{\alpha} = \sqrt{-\alpha^{-2} \Delta + \alpha^{-4} - \alpha^{-1}} \) and \( T^{\alpha} = -\Delta/2 \) when \( \alpha = 0 \).

With \( \nu = Z \), we can evaluate

\[
\text{Tr} \left[ T^{\alpha} - \frac{Z}{|x|} 1_{\{|x|<r\}} \right] \geq -CZ^{5/2}\alpha^{1/2} - C \int_{|x|<r} \left( \frac{Z}{|x|} \right)^{5/2} dx
\]

\[
-C\alpha^{3} \int_{\alpha<|x|} \left( \frac{Z}{|x|} \right)^{4} dx
\]

\[
= -C(Z\alpha)^{1/2}Z^{2} - CZ^{5/2}r^{1/2} - C(Z\alpha)^{2}Z^{2}
\]

\[
\geq -CZ^{2} - CZ^{5/2}r^{1/2}, \quad (A6)
\]
where we have used that $Z\alpha \leq \frac{2}{\pi}$.

With the choice of $r$ of

$$r = Z^{-1/2}n^{2/3} \quad \text{for fermions} \quad \text{(A7)}$$
$$r = Z^{-1} \quad \text{without symmetry,} \quad \text{(A8)}$$

and using that $n \geq 1$, we complete the proof of Lemma 3.

2. Proof of Theorem 4

Using Lemma 3 we can state

$$(\Psi_n, \sum_{i=1}^{n} T_i^\alpha \Psi_n) - Z(\Psi_n, \sum_{i=1}^{n} \frac{1}{|x_i|} \Psi_n) \geq -Z^2 \kappa(n). \quad \text{(A9)}$$

We obtain an estimate on $(\Psi_n, \sum_{i=1}^{n} T_i^\alpha \Psi_n)$ through an assessment of the energy of a single atom

$$0 \geq E^a(n, Z; \alpha) = (\Psi_n, H^a(n, Z; \alpha) \Psi_n) \quad \text{(A10)}$$

$$\geq \varepsilon(\Psi_n, \sum_{i=1}^{n} T_i^\alpha \Psi_n) + (1 - \varepsilon)(\Psi_n, \sum_{i=1}^{n} T_i^\alpha \Psi_n) - (\Psi_n, \sum_{i=1}^{n} \frac{Z}{|x_i|} \Psi_n)$$

$$\geq \varepsilon(\Psi_n, \sum_{i=1}^{n} T_i^\alpha \Psi_n) + (1 - \varepsilon)(\Psi_n, \sum_{i=1}^{n} \left( T_i^\alpha - \frac{Z}{(1 - \varepsilon)|x_i|} \right) \Psi_n)$$

$$\geq \varepsilon(\Psi_n, \sum_{i=1}^{n} T_i^\alpha \Psi_n) - (1 - \varepsilon) \kappa(n) \frac{Z^2}{(1 - \varepsilon)^2}, \quad \text{(A11)}$$

using again Lemma 3 in the last step, asserting that $\frac{Z}{1 - \varepsilon} \alpha \leq \frac{2}{\pi}$ by the assumption of Theorem 4. We can conclude that

$$\left( \Psi_n, \sum_{i=1}^{n} T_i^\alpha \Psi_n \right) \leq \frac{(1 - \varepsilon)^{-1}}{\varepsilon} \kappa(n) Z^2, \quad \text{(A12)}$$

and thereby complete the proof of Theorem 4.
[1] J. P. Solovej, Commun. Math. Phys. 130, 185 (1990).
[2] J. P. Solovej, T. Ø. Sørensen, and W. L. Spitzer, Commun. Pur. Appl. Math. 63, 39 (2010).
[3] R. A. Weder, J. Funct. Anal. 20, 319 (1975).
[4] I. W. Herbst, Commun. Math. Phys. 53, 285 (1977).
[5] E. H. Lieb and H. I. Yau, Commun. Math. Phys. 118, 177 (1988).
[6] R. A. Weder, Ann. Inst. Henri Poincare, Sect. A 20, 211 (1974).
[7] J. G. Conlon, Commun. Math. Phys. 94, 439 (1984).
[8] C. Fefferman and R. de la Lave, Rev. Mat. Iberoam. 2, 119 (1986).
[9] I. Daubechies and E. H. Lieb, Commun. Math. Phys. 90, 497 (1983).
[10] E. H. Lieb, Phys. Rev. A 29, 3018 (1984).
[11] A. Dall’Acqua, T. Ø. Sørensen, and E. Stockmeyer, unpublished.
[12] H. L. Cycon, R. G. Froese, W. Kirsch, and B. Simon, *Schrödinger Operators*, Texts and Monographs in Physics (Springer-Verlag, New York [et. al], 2008), 2nd ed.
[13] W. Thirring, *Quantum Mechanics of Atoms and Molecules*, vol. 3 of *A Course in Mathematical Physics* (Springer-Verlag, New York [et. al], 1981).
[14] I. Daubechies, Commun. Math. Phys. 90, 511 (1983).
[15] R. Benguria, H. Siedentop, and E. Stockmeyer, Ann. Henri Poincare 2, 27 (2001).
[16] T. Ø. Sørensen, J. Math. Phys. 46, 052307 (2005).
[17] E. H. Lieb, Rev. Mod. Phys. 53, 603 (1981).
[18] H. Brezis and E. H. Lieb, Commun. Math. Phys. 65, 231 (1979).
[19] V. J. Ivrii and I. M. Sigal, Ann. Math. 138, 243 (1993).