Dissociation of Homonuclear Relativistic Molecular Ions

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March 8, 2000

Abstract

We give lower bounds to the 'size' of diatomic homonuclear relativistic molecules which are modeled by the Herbst operator. We also show that – as in the non-relativistic case – the absence of sufficiently many electrons leads to the dissociation of the molecule.

To obtain these results we found new bounds for the localization error in the semi-relativistic approach.

1 Introduction

Experimentally atoms and molecules are known to have only finitely many electrons. E.g., experimentally doubly charged negative stable ions are not known. It is a mathematical challenge to show this physical fact. It has been conjectured since several years that the charge exceeding the electrically neutral molecule should be bounded by a universal constant times the number of nuclei involved. This is an unresolved question. However, many results in this direction have been obtained in the context of non-relativistic quantum mechanics, among them Lieb [5]. On the other hand it is physically obvious that – for molecules – the number of electrons cannot be too low either, since the Coulomb forces would drive the nuclei apart. A pioneering work in this direction has been done by Ruskai [10]. Later improvements are due to Solovej [11] and Alarcón et al [2]. In particular the last mentioned paper gives an upper bound on the nuclear charges of a homonuclear diatomic molecule. – The purpose of this paper is an extension of the result Alarcón et al to the case when the underlying dynamics is no longer non-relativistic but relativistic. For definiteness we now define the model to be treated, namely the (pseudo)-relativistic Herbst Hamiltonian H_R of N spinless electrons of mass m and charge $-e$ in the field of two nuclei with the same nuclear charge Ze separated by a distance $2R$:

$$\begin{aligned} H_R = &\sum_{i=1}^{N} \left(\sqrt{-\hbar^2 c^2 \Delta_i + m^2 c^4} - \frac{Z\alpha}{|\mathbf{x}_i - \mathbf{R}|} - \frac{Z\alpha}{|\mathbf{x}_i + \mathbf{R}|} \right) \\ &+ \sum_{1 \leq i < j \leq N} \frac{\alpha}{|\mathbf{x}_i - \mathbf{x}_j|} + \frac{Z^2\alpha}{2R}, \end{aligned} \tag{1}$$

which is selfadjointly realized in $L^2(\mathbb{R}^3)$ and where $\mathbf{R} = (R, 0, 0)$ is the location of one nucleus and $\alpha = e^2/(\hbar c)$ is the Sommerfeld fine structure constant having the physical value of about $1/137$. The lowest occurring energy for a given distance $2R$ between the nuclei is

$$E(R) = \inf\{(\psi, H_R\psi) \mid \psi \in C_0^\infty(\mathbb{R}^{3N}), \|\psi\| = 1\}. \tag{2}$$

Note that we do disregard any symmetry of the underlying state space, i.e., we look at boltzonic electrons, i.e., particles for which there is no requirement on the symmetry of the states which have the same ground state energy as bosonic atoms. The ground state energy E is given by

$$E = \inf\{E(R) \mid R > 0\}. \tag{3}$$

The binding energy of the molecule is defined as the ground state energy of H_R minus the energy of the split system.

$$E_{\mathrm{b}}(N, R, Z) = \inf\{\inf E(R) | R > 0\} - E_s \tag{4}$$

where E_s is the lowest energy that results from separating the systems into two parts. The molecule dissociates (is instable), if E_b is nonnegative. Since this condition is independent of the mass (for $m > 0$), we use $m = 1$ in the following.

The structure of the paper is as follows: In Section 2 we give a minimal distance for the nuclei of a stable molecule. Technically this is expressed in Lemma 1.

In Section 3 we use Lemma 1 to find a lower bound on the nuclear charge beyond which one electron diatomic molecules dissociate.

Finally, in Section 4 we use all the results above to find a lower bound on Z/N in the general N electron case.

2 A Lower Bound on the Size of the Molecule

Lemma 1. *Consider a diatomic homonuclear molecule. The nuclei of atomic number Z are located at $\mathbf{R} = (R, 0, 0)$ and $-\mathbf{R}$. If $E(R)$ as defined in (2) has a minimum at $R_0 > 0$ and $Z\alpha < \frac{1}{4}$, then*

$$R_0 \geq \frac{Z^2\alpha}{2N}[1 - [1 + \frac{(Z\alpha)^2}{[\frac{1}{4} + \sqrt{\frac{1}{16} - (Z\alpha)^2}]^2}]^{\frac{-1}{2}}]^{-1}. \tag{5}$$

Note that we are working in units where $m = \hbar = c = 1$, i.e., $\alpha = e^2$.

Proof. The Hamiltonian that describes the molecule is given by (1). The key ingredients in our proof are the Feynman-Hellmann formula, the virial theorem for the Herbst operator, the Rayleigh-Ritz principle and the estimate from below for the ground state of a hydrogenic atom by Martin and Roy [7]. For a shorthand notation let $\mathbf{x} \in \mathbb{R}^{3N}$ be the vector $(\mathbf{x}_1, \mathbf{x}_2, \ldots, \mathbf{x}_N)$ and

$$V(\mathbf{x}) = \sum_{i=1}^{N} \left(-\frac{Z\alpha}{|\mathbf{x}_i - R\hat{\mathbf{n}}|} - \frac{Z\alpha}{|\mathbf{x}_i + R\hat{\mathbf{n}}|} \right) + \sum_{1 \leq i < j \leq N} \frac{\alpha}{|\mathbf{x}_i - \mathbf{x}_j|}. \tag{6}$$

We denote by

$$\mathbf{x} \cdot \nabla_{\mathbf{x}} V = \sum_{i=1}^{N} \mathbf{x}_i \cdot \nabla_{x_i} V. \tag{7}$$

It is simple to check the following identity:

$$\frac{1}{R}(\mathbf{x} \cdot \nabla V + V) = \sum_{i=1}^{N} [\frac{Z\alpha}{|\mathbf{x}_i - R\hat{\mathbf{n}}|^3}(\mathbf{x}_i - R\hat{\mathbf{n}}) \cdot \hat{\mathbf{n}} - \frac{Z\alpha}{|\mathbf{x}_i + R\hat{\mathbf{n}}|^3}(\mathbf{x}_i + R\hat{\mathbf{n}}) \cdot \hat{\mathbf{n}}]. \tag{8}$$

Now, let ψ denote the ground state of H. Using the Feynman–Hellmann formula, we have

$$\frac{\partial E(R)}{\partial R} = -\frac{Z^2\alpha}{2R^2} + \left(\psi, \sum_{i=1}^{N}[-\frac{Z\alpha}{|\mathbf{x}_i - R\hat{\mathbf{n}}|^3}(\mathbf{x}_i - R\hat{\mathbf{n}})\cdot\hat{\mathbf{n}} + \frac{Z\alpha}{|\mathbf{x}_i + R\hat{\mathbf{n}}|^3}(\mathbf{x}_i + R\hat{\mathbf{n}})\cdot\hat{\mathbf{n}}]\psi\right). \quad (9)$$

¿From (8) and (9) we have

$$\frac{\partial E(R)}{\partial R} = -\frac{Z^2\alpha}{2R^2} - \frac{1}{R}\left(\psi, (\mathbf{x}\cdot\nabla V + V)\psi\right). \quad (10)$$

According to Herbst [4], Theorem 2.4, the following Virial Theorem holds

$$(\psi, \mathbf{x}\cdot\nabla V\psi) = \sum_{i=1}^{N}\left(\psi, \frac{\mathbf{p}_i\cdot\mathbf{p}_i}{\sqrt{\mathbf{p}_i{}^2+1}}\psi\right). \quad (11)$$

As quadratic forms,

$$\frac{\mathbf{p}_i\cdot\mathbf{p}_i}{\sqrt{\mathbf{p}_i{}^2+1}} \geq \sqrt{\mathbf{p}_i{}^2+1} - 1 \equiv K_i. \quad (12)$$

Combining (10), (11) and (12) we get

$$\frac{\partial E(R)}{\partial R} \leq -\frac{Z^2\alpha}{2R^2} - \frac{1}{R}\sum_{i=1}^{N}(\psi, K_i\psi) - \frac{1}{R}(\psi, V\psi). \quad (13)$$

However,

$$(\psi, V\psi) \geq \sum_{i=1}^{N}\left(\psi, [-\frac{Z\alpha}{|\mathbf{x}_i - R\hat{\mathbf{n}}|} - \frac{Z\alpha}{|\mathbf{x}_i + R\hat{\mathbf{n}}|}]\psi\right). \quad (14)$$

Using (13) and (14) we get

$$\frac{\partial E(R)}{\partial R} \leq -\frac{Z^2\alpha}{2R^2} - \frac{1}{2R}\sum_{i=1}^{N}\left(\psi, [K_i - \frac{2Z\alpha}{|\mathbf{x}_i - R\hat{\mathbf{n}}|} + K_i - \frac{2Z\alpha}{|\mathbf{x}_i + R\hat{\mathbf{n}}|}]\psi\right). \quad (15)$$

At this point we note that the lowest eigenvalues of the hydrogenic Herbst operator in each angular momentum channel are bounded from below by the corresponding one of the Klein-Gordon operator (Martin and Roy [7]). The latter are known explicitly.

Since $K_i - \frac{2Z\alpha}{|\mathbf{x}_i - R\hat{\mathbf{n}}|}$ is just the Herbst operator for a hydrogenic atom (Herbst [4]) of charge $2Z$ located at R (location does not matter any more), we have, using the Rayleigh-Ritz principle and following Martin and Roy that

$$-(\psi, K_i - \frac{2Z\alpha}{|\mathbf{x}_i - R\hat{\mathbf{n}}|}\psi) \leq 1 - \frac{1}{\sqrt{1 + \frac{(Z\alpha)^2}{[\frac{1}{4}+\sqrt{\frac{1}{16}-(Z\alpha)^2}]^2}}}. \tag{16}$$

Finally, from (15) and (16)

$$\frac{\partial E(R)}{\partial R} \leq -\frac{1}{2R^2}[Z^2\alpha - 2RN(1 - \frac{1}{\sqrt{1 + \frac{(Z\alpha)^2}{[\frac{1}{4}+\sqrt{\frac{1}{16}-(Z\alpha)^2}]^2}}})]. \tag{17}$$

Hence if,

$$R \leq \frac{Z^2\alpha}{2N}[1 - [1 + \frac{(Z\alpha)^2}{[\frac{1}{4} + \sqrt{\frac{1}{16} - (Z\alpha)^2}]^2}]^{\frac{-1}{2}}]^{-1}, \tag{18}$$

and $Z\alpha < \frac{1}{4}$, we have $\frac{\partial E(R)}{\partial R} \leq 0$. □

Remark 1.

- *The equation* (5) *is monotonically decreasing as a function of* Z *and has a minimum at* $Z\alpha = \frac{1}{4}$*, thus* $RN \geq 14.617$ *for all* $Z\alpha < \frac{1}{4}$.
- *Observe that* $\frac{\partial E_b(R)}{\partial R} = \frac{\partial E(R)}{\partial R}$*, since the energy of each of the two individual atoms gotten from the splitting of the molecule does not depend on* R.
- *Notice also that we have treated the electrons as bosons when estimating* (15) *using* (16).
- *Because of the contraint* $Z\alpha < \frac{1}{4}$*, the lemma is not so much an asymptotic estimate on the size of a molecule (as in [11] or in [1]) but a tool for use in subsequent estimates later.*

3 The One-Electron Molecule

To demonstrate the strategy to obtain an upper bound minimal nuclear charge that prevents binding for the homonuclear diatomic molecule, we will begin with the simplest case, i.e., one electron whose kinetic energy is given by the naive quantization of the classical relativistic Hamiltonian.

Theorem 1. *Consider a diatomic molecule with homonuclear nuclei with only one electron. Then instability occurs when*

$$2.864 \leq Z < \frac{1}{4\alpha}. \tag{19}$$

Proof. In this situation the Hamiltonian is just

$$H_R = \sqrt{-\Delta+1} - 1 - \frac{Z\alpha}{|\mathbf{x}-\mathbf{R}|} - \frac{Z\alpha}{|\mathbf{x}+\mathbf{R}|} + \frac{Z^2\alpha}{2R}, \tag{20}$$

and the lowest occurring energy of the separated systems is given by

$$E_s = \inf\sigma(\sqrt{-\Delta+1} - 1 - Z\alpha/|\mathbf{x}|).$$

To treat this operator we follow the general strategy of Solovej [11] (see also Alarcón et al [2]): Firstly we localize the nuclei in two half spaces and bound the electron-nuclei singularity. Secondly we use the bound on the minimal distance between the nuclei to estimate the localization error. Because of the non-local nature of the kinetic energy operator this requires some extra care.

Pick two localizing functions $\chi_1, \chi_2 : \mathbb{R}^3 \to [0,1]$, $\chi_1(\mathbf{x}) := \cos(\psi(x_1/R))$ and $\chi_2(\mathbf{x}) := \sin(\psi(x_1/R))$ with

$$\psi(t) := \begin{cases} 0 & t < -1 \\ \frac{\pi}{4}(1+t) & t \in [-1,1] \\ \frac{\pi}{2} & t > 1 \end{cases}. \tag{21}$$

Obviously these two functions form a Lipschitz continuous partition of unity. Note also that $\chi_2(t) = \chi_1(-t)$ holds with this choice. Localizing with these functions yields

$$\begin{aligned}(\psi, H_R\psi) \quad = \quad & (\psi, \chi_1(\sqrt{-\Delta+1} - 1 - \frac{Z\alpha}{|\cdot+\mathbf{R}|})\chi_1\psi) \\ & +(\psi, \chi_2(\sqrt{-\Delta+1} - 1 - \frac{Z\alpha}{|\cdot-\mathbf{R}|})\chi_2\psi) \\ & -(\psi, L\psi) + \frac{Z^2\alpha}{2R} - Z\alpha(\psi, (\frac{\chi_1^2}{|\cdot-\mathbf{R}|} + \frac{\chi_2^2}{|\cdot+\mathbf{R}|})\psi),\end{aligned} \tag{22}$$

where L is the localization error and has the kernel

$$L(\mathbf{x},\mathbf{y}) = \frac{K_2(|\mathbf{x}-\mathbf{y}|)\sin^2((\psi(x_1)-\psi(y_1))/(2R))}{\pi^2|\mathbf{x}-\mathbf{y}|^2} \tag{23}$$

(Lieb and Yau [6]) where $K_2(x)$ is a modified Bessel function (see [8]). Estimating the operators sandwiched between the χ_j in the first two lines of (22) from below by E_s and observing that $\chi_1^2 + \chi_2^2 = 1$ we get

$$(\psi, H_R\psi) - E_s \geq -(\psi, L\psi) + \frac{Z^2\alpha}{2R} - Z\alpha(\psi, (\frac{\chi_1^2}{|\cdot-\mathbf{R}|} + \frac{\chi_2^2}{|\cdot+\mathbf{R}|})\psi). \tag{24}$$

First we use the fact that (see Appendix A for the proof)

$$Z\alpha(\psi, (\frac{\chi_1^2}{|\mathbf{x}-\mathbf{R}|} + \frac{\chi_2^2}{|\mathbf{x}+\mathbf{R}|})\psi) \leq \frac{Z\alpha}{R}, \tag{25}$$

yielding the following equation for instability

$$E_b \geq -(\psi, L\psi) + \frac{Z^2\alpha}{2R} - \frac{Z\alpha}{R}. \tag{26}$$

Next we estimate the localization error. Using the Schwarz inequality we get that

$$(\psi, L\psi) \leq \max_{x_1 \in \mathbb{R}} \varphi_L(x_1) \tag{27}$$

where

$$\varphi_L(x_1) := \int_{\mathbb{R}^3} L(\mathbf{x}, \mathbf{y}) d\mathbf{y}. \tag{28}$$

For shorthand notation we define,

$$S(s,t) := 4\sin^2((\psi(s) - \psi(t))/2). \tag{29}$$

Now we use cylindrical coordinates, choosing the line joining the nuclei as the first coordinate axis. We have

$$\varphi_L(x_1) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dy_1 \left\{ \int_0^{\infty} \rho d\rho \frac{K_2(\sqrt{(x_1-y_1)^2+\rho^2})}{(x_1-y_1)^2+\rho^2} \right\} S(\frac{x_1}{R}, \frac{y_1}{R}). \tag{30}$$

Using [3], Formula 6.596.3, we can compute the expression in { } and obtain

$$\varphi_L(x_1) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dy_1 \frac{K_1(|x_1-y_1|)}{|x_1-y_1|} S(\frac{x_1}{R}, \frac{y_1}{R}). \tag{31}$$

Changing of variables, $u \equiv x_1/R$ and $v \equiv y_1/R$ we get,

$$\varphi_L(Ru) = \frac{1}{2\pi}\int_{-\infty}^{\infty} dv \frac{K_1(R|u-v|)}{|u-v|} S(u,v). \tag{32}$$

Using the fact that the equation above has a maximum at $u = 0$ (for the proof see Appendix B) and the choice of the χ_j in (21) we obtain

$$(\psi, L\psi) \leq \frac{2}{\pi}\left\{(1 - \frac{\sqrt{2}}{2})\int_1^{\infty} \frac{K_1(Rv)}{v} dv + \int_0^1 \frac{K_1(Rv)}{v}(1 - \cos(\frac{\pi}{4}v))dv\right\}. \tag{33}$$

Estimating the integrals

$$\int_1^{\infty} \frac{K_1(Rv)}{v} dv \leq \int_1^{\infty} K_1(Rv) dv = \frac{1}{R} K_0(R), \tag{34}$$

and

$$I := \int_0^1 \frac{K_1(Rv)}{v}(1 - \cos\left(\frac{\pi}{4}v\right))dv = \int_0^1 K_1(Rv)\left(\frac{\pi^2 v}{32}\cos(\frac{\pi}{4}w)\right) dv, \tag{35}$$

where $w \in (0,1)$, and using the Taylor expansion for the cosine we get

$$I \leq \frac{\pi^2}{32} \int_0^1 dv K_1(Rv) v \leq \frac{\pi^2}{32} \int_0^\infty dv K_1(Rv) v \leq \frac{\pi^3}{64R^2}. \tag{36}$$

So finally we have that,

$$(\psi, L\psi) \leq \frac{1}{R} \left(\frac{2}{\pi}\right) \left\{ (1 - \frac{\sqrt{2}}{2}) K_0(R) + \frac{\pi^3}{64R} \right\} := \frac{G(R)}{R}. \tag{37}$$

Note that G is a decreasing function implying that $(\psi, L\psi) \leq \frac{G(R_0)}{R}$, where R_0 is the lower bound for R that we found in Lemma 1. To obtain a numerical value, we will suppose that $Z \leq 3$. We then get that $R_0 \geq 34.17$ and we arrive to

$$(\psi, L\psi) \leq \frac{0.009026}{R}. \tag{38}$$

Now using (38) to estimate (26) we hav

$$E_b \geq -\frac{0.009026}{R} + \frac{Z^2\alpha}{2R} - \frac{Z\alpha}{R} \geq 0, \tag{39}$$

where the last inequality holds only if $Z \geq 2.864$. □

Remark 2. *Notice that estimate implies* (24) *that the molecule dissociates, i.e.* $E_b \geq 0$, *when* Z *is big enough and* $R \geq R_0$. *This is also true, if* $Z\alpha < \frac{1}{4}$, *when* $R < R_0$ *because* $\frac{\partial E_b}{\partial R} \leq 0$ *by Lemma 1.*

4 The N Electron Case

Theorem 2. *For the* N *electron diatomic molecule we have dissociation (i.e.* $E_b \geq 0$*) under either of the following conditions on* Z *and* N*:*
a) $Z \geq N(1 + \sqrt{1 + \frac{a}{\alpha N}})$, *with* $a = 0.7587$.
b) $\frac{Z}{N} \geq \min\left\{1 + \sqrt{1 + \frac{a}{\alpha N}},\ b\right\}$, *and* $Z\alpha < \frac{1}{4}$ *where* $a = 0.7587$, *as before, and* $b = 3.9$.

Proof. Consider the two cluster decomposition $\beta = (\beta_1, \beta_2)$ of $\{1, .., N\}$. The inter-cluster potential is given by,

$$I_\beta = \sum_{i \in \beta_2} \frac{-Z\alpha}{|\mathbf{x}_i + \mathbf{R}|} + \sum_{i \in \beta_1} \frac{-Z\alpha}{|\mathbf{x}_i - \mathbf{R}|} + \sum_{i \in \beta_1} \sum_{j \in \beta_2} \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|} + \frac{Z^2\alpha}{2R}. \tag{40}$$

We define the cluster Hamiltonian $H_\beta = H - I_\beta$. Let ψ be the ground state of H and let $E_\beta = inf(\sigma(H_\beta))$ then the instability condition is given by,

$$E \geq \min_\beta E_\beta = E_s. \tag{41}$$

The partition of unity is defined as,

$$J_\beta(\mathbf{x}) = \prod_{i\in\beta_1} \chi_1(\mathbf{x}_i) \prod_{j\in\beta_2} \chi_2(\mathbf{x}_j). \tag{42}$$

Now noting that $\sum_\beta J_\beta(\mathbf{x})^2 = 1$ we insert this in the expectation value of the Hamiltonian,

$$(\psi, H_R\psi) = (\psi, (\sum_\beta J_\beta H_R J_\beta)\psi) - (\psi, (\sum_\beta J_\beta [H_R, J_\beta])\psi), \tag{43}$$

and observe that

$$\sum_\beta J_\beta[J_\beta, H_R] = \sum_\beta J_\beta[\sum_{k=1}^N \sqrt{-\Delta_k + 1}, J_\beta] = \sum_{k=1}^N \sum_{j=1}^2 \chi_j(\mathbf{x}_k)[\sqrt{-\Delta_k+1}, \chi_j(\mathbf{x}_k)], \tag{44}$$

then

$$(\psi, (\sum_\beta J_\beta[H_R, J_\beta])\psi) = N(\psi, L\psi) \tag{45}$$

where the kernel of L was given in (23). Then we have

$$\begin{aligned} (\psi, H\psi) &= (\psi, (\sum_\beta J_\beta H_\beta J_\beta)\psi) + \sum_\beta (\psi, (J_\beta^2 I_\beta)\psi) - N(\psi, L\psi) & (46) \\ &\geq \sum_\beta E_\beta(\psi, J_\beta^2\psi) + \sum_\beta(\psi, (J_\beta^2 I_\beta)\psi) - N(\psi, L\psi) & (47) \\ &\geq E_s + \sum_\beta (\psi, (J_\beta^2 I_\beta)\psi) - N(\psi, L\psi). & (48) \end{aligned}$$

Furthermore,

$$\begin{aligned} \sum_\beta (\psi, (J_\beta^2 I_\beta)\psi) &\geq -Z\alpha \sum_{i=1}^N (\psi, (\frac{\chi_1^2(\mathbf{x}_i)}{|\mathbf{x}_i - \mathbf{R}|} + \frac{\chi_2^2(\mathbf{x}_i)}{|\mathbf{x}_i + \mathbf{R}|})\psi) + \frac{Z^2\alpha}{2R} \\ &\geq -\frac{Z\alpha N}{R} + \frac{Z^2\alpha}{2R}. \end{aligned} \tag{49}$$

Here we have dropped the inter-electronic potential and used (25). Then we obtain

$$E_b = (\psi, H\psi) - E_s \geq -N(\psi, L\psi) - \frac{Z\alpha N}{R} + \frac{Z^2\alpha}{2R} \geq 0, \tag{50}$$

where the last inequality can be written as,

$$\frac{\tilde{Z}^2\alpha}{2} - \tilde{Z}\alpha - \frac{R}{N}(\psi, L\psi) \geq 0, \tag{51}$$

where $\tilde{Z} \equiv Z/N$. At this point we will bound the localization error in two different ways yielding, through equation (51), the conditions a) and b) of the theorem. We start with the $1/R$ behavior. Observing that the Bessel function K_1 obeys the estimate $K_1(x) \leq 1/x$ for positive x (see Appendix B) we get

$$\int_1^\infty \frac{K_1(Rv)}{v} dv \leq \frac{1}{R} \int_1^\infty \frac{1}{v^2} dv = \frac{1}{R}, \tag{52}$$

and moreover

$$\int_0^1 \frac{K_1(Rv)}{v} (1 - \cos\left(\frac{\pi}{4}v\right)) dv \leq \frac{1}{R} \int_0^1 \frac{(1 - \cos\left(\frac{\pi}{4}v\right))}{v^2} dv \leq 0.303/R. \tag{53}$$

Thus $R(\psi, L\psi) \leq 0.3793$, and using this to bound (51) we obtain that for instability we need

$$\tilde{Z} \geq 1 + \sqrt{1 + \frac{0.7587}{\alpha N}}, \tag{54}$$

which is condition a).

Finally for the $1/R^2$ behavior, we just use (37), that is

$$(\psi, L\psi) \leq \frac{1}{R^2} \left(\frac{2}{\pi}\right) \left\{ (1 - \frac{\sqrt{2}}{2}) R K_0(R) + \frac{\pi^3}{64} \right\} \leq \frac{0.3954}{R^2}, \tag{55}$$

since $xK_0(x) \leq 0.4665$. Then for instability $\tilde{Z} \geq 1 + \sqrt{1 + \frac{0.7908}{\alpha R N}}$. If we restrict ourselves to $Z\alpha < 1/4$, we need only consider values of $RN \geq 14.617$ (see Remarks 1 and 2 above). Therefore, we have dissociation if $\tilde{Z} \geq 3.900$. This together with (54) is condition b). □

A

To prove the equation (25) we first introduce

$$F(\mathbf{t}) := \frac{1}{R} \left\{ \frac{\cos(\psi(t_1))^2}{\sqrt{(t_1 - 1)^2 + {t_2}^2 + {t_3}^2}} + \frac{\sin(\psi(t_1))^2}{\sqrt{(t_1 + 1)^2 + {t_2}^2 + {t_3}^2}} \right\}. \tag{56}$$

For $t_1 \leq -1$ we find that

$$F(\mathbf{t}) = \frac{1}{R} \frac{1}{\sqrt{(t_1 - 1)^2 + {t_2}^2 + {t_3}^2}} \leq \frac{1}{|t_1 - 1|} \leq \frac{1}{R}. \tag{57}$$

Similarly we get $F(\mathbf{t}) \leq 1/R$ for $t_1 \geq 1$. For $t_1 \in (-1, 1)$ we obtain

$$F(\mathbf{t}) \leq \frac{1}{R} \left\{ \frac{\cos(\psi(t_1))^2}{(1 - t_1)} + \frac{\sin(\psi(t_1))^2}{1 + t_1} \right\} \leq \frac{1}{R}. \tag{58}$$

The last inequality holds because the function in the braces is a positive concave even function on $(-1, 1)$ with maximum at $t_1 = 0$ and value 1 at this point. So the equation (25) is proved by taking $\mathbf{t} := \mathbf{x}/R$.

B

To prove that the maximum of the bound for the localization error occurs at $u = 0$ we first observe that

$$\begin{aligned} \varphi_L(Ru) =& \frac{1}{2\pi} \int_{-\infty}^{\infty} dv \frac{K_1(R|u-v|)}{|u-v|} S(u,v) \\ =& \frac{2}{\pi} \int_{-\infty}^{\infty} dv \frac{K_1(R|u-v|)}{|u-v|} \sin^2[(\psi(u) - \psi(v))/2], \end{aligned} \tag{59}$$

where ψ is defined in (21). We start with some simple facts.

Proposition 1. *The following is true:*

1. *$K_1(x) \leq 1/x$ for positive x.*
2. *$\varphi_L(u) = \varphi_L(-u)$ for all $u \in \mathbb{R}$.*

Proof.

1. Set $f(x) := xK_1(x)$. The proof is immediate from the observation that $\lim_{x\to 0} f(x) = 1$ and that $f'(x) < 0$ for positive x.

2. Let $g(u,v) := K_1(R|u-v|)S(u,v)/|u-v|$. The function g fulfills $g(u,v) = g(-u,-v)$. Changing the variable in the integral $v := -s$ yields the desired result. □

We will now turn to the main goal of this section, namely proving that the function φ_L has its maximum at zero. We will start with the massless case and extend the result to the general massive case. In the latter it is enough for us to assume $R \geq 1$.

B.1 The Massless Case

Lemma 2. *Υ has a unique maximum at $u = 0$ where*

$$\Upsilon(u) := \int_{-\infty}^{\infty} dv \frac{\sin^2[(\psi(u) - \psi(v))/2]}{(u-v)^2}$$

and ψ as defined in (21).

Proof. Let first suppose that $u \in [0, 1)$, we start noting that

$$\Upsilon(u) = \int_{-\infty}^{\infty} dv \frac{\sin^2[(\psi(u) - \psi(v+u))/2]}{v^2}.$$

Taking the derivative of Υ and separating the integral using (21) we get

$$\begin{aligned}\Upsilon'(u) =& \frac{\pi}{4}\left\{\sin(\psi(u))\int_{1+u}^{\infty}\frac{dv}{v^2} - \cos(\psi(u))\int_{1-u}^{\infty}\frac{dv}{v^2}\right\} \\ =& \frac{\pi\left[(1-u)\sin(\psi(u)) - (1+u)\cos(\psi(u))\right]}{4(1-u^2)}.\end{aligned} \tag{60}$$

It is clear that $\Upsilon'(0) = 0$. Moreover, $\Upsilon'(u) \leq 0$ for $u \in (0,1)$ since the function between [ ] in the last equation is convex in $(0,1)$ and vanishes at $u = 0$ and $u = 1$. Hence the maximum of Υ on $[0,1)$ occurs at 0.

To extend the same result for any u we consider the extension of the second statement of Proposition 1 for the massless case and observe that for $u \geq 1$

$$\Upsilon(u) = \frac{1}{2}\int_{-\infty}^{-1}\frac{dv}{(u-v)^2} + \int_{-1}^{1} dv \frac{\sin(\frac{\pi}{8}(v-1))^2}{(u-v)^2},$$

is a decreasing function of u.This together with the continuity of I proves the lemma. □

B.2 The Massive Case

We will enunciate first some facts.

Proposition 2. *Let*

$$\Upsilon_R(u) := \int_{-\infty}^{\infty} dv \frac{K_1(R|u-v|)}{|u-v|}\sin^2[(\psi(u) - \psi(v))/2],$$

and $R \geq 1$. Then the following is true:

1. *The derivative with respect to u fulfills, $\Upsilon_R'(u) \leq \Upsilon_{R=1}'(u) := \Upsilon_1'(u)$ for all $u \in [0,1)$.*
2. *$K_1(u) \geq e^{-u}/u$ for all positive u.*
3. *$K_0(u+1) \leq 5e^{-(u+1)}/4$ for all non-negative u.*

Proof.

1. Using the same procedure as in Lemma 2 we obtain that for $u \in [0,1)$

$$\Upsilon_R'(u) = \frac{\pi}{4}\left(\sin(\psi(u))\int_{R(1+u)}^{\infty}\frac{K_1(v)}{v}dv - \cos(\psi(u))\int_{R(1-u)}^{\infty}\frac{K_1(v)}{v}dv\right), \tag{61}$$

and then deriving with respect to R we see that the function Υ_R' is decreasing as R increase for $R > 0$ and $u \in [0,1)$.

2. Let $f(u) := uK_1(u)e^u$. We see that $f(0) = 1$ and the derivative $f'(u) = ue^u(K_1(u) - K_0(u)) \geq 0$ for all $u \in (0,\infty)$.

3. The same idea as in 2. shows that $g(0) < 1$ and $g'(u) \leq 0$ on $u \in [0,\infty)$ where $g(u) := \frac{4}{5}K_0(1+u)e^{(1+u)}$. □

Lemma 3. *Assume Υ_R as in Proposition 2 and $R \geq 1$ then Υ_R has a unique maximum at $u = 0$.*

Proof. First we prove the claim for $u \in [0, 1)$, we note that by (61) $u = 0$ is a critical point. Considering Proposition 2.1 it suffices to prove that $\Upsilon_1'(u) \leq 0$. Now, using Proposition 2.2 and (61) we get

$$\begin{aligned}
\Upsilon_1'(u) &\leq (\sin(\psi(u)) - \cos(\psi(u))) \int_{1+u}^{\infty} \frac{K_1(v)}{v} dv - \cos(\psi(u)) \int_{1-u}^{1+u} \frac{K_1(v)}{v} dv \\
&\leq \frac{(\sin(\psi(u)) - \cos(\psi(u)))}{1+u} \int_{1+u}^{\infty} K_1(v) dv - \cos(\psi(u)) \int_{1-u}^{1+u} \frac{e^{-v}}{v^2} dv \\
&\leq \frac{(\sin(\psi(u)) - \cos(\psi(u)))}{1+u} K_0(1+u) - \cos(\psi(u)) e^{-(1+u)} \left(\frac{1}{1-u} - \frac{1}{1+u} \right) \\
&= \frac{K_0(1+u) \left[\sin(\psi(u)) - u \sin(\psi(u)) - \cos(\psi(u)) + u \cos(\psi(u)) \right]}{1-u^2} \\
&- \frac{2u e^{-(1+u)} \cos(\psi(u))}{1-u^2}.
\end{aligned}$$

Denote the expression in the numerator of the last equation by $h(u)$. It is enough to prove that $h(u) \leq 0$ for $u \in [0, 1)$. Using the third statement of Proposition 2 we arrive at

$$h(u) \leq e^{-(u+1)} \left[\frac{5}{4} \sin(\psi(u)) - \frac{5u}{4} \sin(\psi(u)) - \frac{5}{4} \cos(\psi(u)) - \frac{3u}{4} \cos(\psi(u)) \right] \leq 0,$$

the last inequality holds for all $u \in [0, 1)$, and the lemma is proved for this domain. To extend our proof for all real u we use the second statement of Proposition 1 and that for $u \geq 1$

$$\Upsilon_R(u) = \sin(\frac{\pi}{4})^2 \int_{-\infty}^{-1} \frac{K_1(R(u-v))}{u-v} dv + \int_{-1}^{1} dv \frac{K_1(R(u-v))}{u-v} \sin^2 \frac{\pi(v-1)}{8}.$$

Here clearly $\Upsilon_R(u) \leq \Upsilon_1(u)$. Noting that the derivative of $K_1(u-v)/(u-v)$ with respect to u is $-[2K_1(u-v) + (u-v)K_0(u-v)]/(u-v)^2$ non-positive for $u \geq 1$ and that $v < 1$, we conclude that in this domain Υ_R has its maximum at 1. These facts and the continuity of Υ_R prove the lemma. □

Acknovledgement: R. B. acknowledges partial support of the project by FONDECYT (Chile), project 199-0427; E. S. thanks CONICYT (Chile) for support through a doctoral fellowship. All authors acknowledge support by the Volkswagen Stiftung for a cooperation grant. We also are thankful for the hospitality by our partner institutions.

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