

ANNALES DE L'I. H. P., SECTION A

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Annales de l'I. H. P., section A, tome 52, n° 4 (1990), p. 397-414

http://www.numdam.org/item?id=AIHPA_1990__52_4_397_0

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Limit on the excess negative charge of a dynamic diatomic molecule

by

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ABSTRACT. — It is shown that the excess negative charge of a diatomic molecule consisting of N electrons and two dynamic nuclei with charges Z_1 and Z_2 is bounded above by a constant times the total nuclear charge. The nuclear motion is completely unrestricted; and the kinetic energy of nuclei with realistically finite mass is included in the Hamiltonian.

RÉSUMÉ. — Nous montrons que la charge négative en excès d'une molécule diatomique formée de N électrons et de deux noyaux mobiles de charges Z_1 et Z_2 est bornée supérieurement par un facteur proportionnel à la charge nucléaire totale. Le mouvement des noyaux est sans contraintes, et nous incluons un terme d'énergie cinétique des noyaux avec une masse finie.

⁽¹⁾ Research supported in part by NSF grant DMS-8808112.

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I. INTRODUCTION

For atomic systems, it is well-known that all positive ions are so stable that they have infinitely many bound states ([1]-[4]), but that extremely negative ions are unstable with respect to expulsion of at least one electron. The first proof of the latter result was given in 1982, independently by Ruskai [5] and by Sigal [6]. Subsequently, Sigal [7], Lieb [8], and others ([9]-[11]) found improved estimates on the maximum number of electrons that a nucleus could bind. For molecular systems, it was shown ([5], [8]) that similar results hold in the fixed nuclei, or infinite mass, approximation. However, these proofs are not valid in the more realistic case of nuclei with finite mass.

Moreover, when the nuclei are not fixed, the situation for positive ions is quite different; a molecule will be unstable if the nuclear charges are much greater than the total electronic charge. A proof of this phenomenon was recently given [12] for diatomic molecules, which are unstable with respect to breakup into two atomic subsystems when both nuclear charges are large compared to the number of electrons; an alternate proof has recently been reported by Solovej [13]. In this paper it is shown that the techniques developed in [12] for positive molecular ions can also be used to obtain a bound on the excess negative charge of a diatomic molecule in which the nuclei are allowed to be completely dynamic.

Let H be the Hamiltonian for a diatomic molecule with N electrons, nuclear charges Z_1 and Z_2 , and nuclear masses M_k satisfying $M_k = Z_k M_0$, where M_0 is constant. Our goal is to prove the following.

THEOREM. — *For every pair of integers Z_1 and Z_2 , there exists a constant $N^c > 0$ such that whenever the number of electrons $N > N^c$, then H has no discrete spectrum. Furthermore, $N^c < \eta (Z_1 + Z_2)$ for some constant η .*

The proof uses the localization or “geometric” techniques employed in other bound state problems; these techniques are discussed in Cycon *et al.* [14]. In the region where at least one electron is far from both nuclei, the previous atomic results can be applied to an effective charge $-2(Z_1 + Z_2)$; when every electron is as close to one nucleus as the nuclei are to each other, the partition of unity developed in [12] for the positive molecules can be used, provided one can estimate the energy cost of adding excess electrons to an atom and confining this subsystem to a ball of finite radius. Such estimates can be obtained in several ways; a modification of the localization proofs ([5]-[7], [14]) that an atom cannot bind too many electrons is presented here. Finally, in order to control the localization errors, one must also show that the nuclei and/or electrons cannot be confined to a very small region.

Although the assumption $M_k = Z_k M_0$ is not absolutely necessary, control of the localization error requires that the nuclear masses grow at least as

fast as the charges. In the case of small nuclear charges, one must also assume that the proton/electron mass ratio has a realistic value of $M_0/m \approx 1,000$ to insure that the proof is valid for all homonuclear molecules. Very unbalanced charge ratios, *i. e.* $Z_1 \gg Z_2$, can only be handled when at least one of the charges is relatively large [see (35) and discussion following]. There are special subtleties when the smaller charge is 1, so that the result may not be applicable to a few practical situations, *e. g.*, HF (hydrogen fluoride).

The bounds presented at the end of section III are obviously far from optimal; Lieb [8] showed that $N^c < 2(Z_1 + Z_2 + 1)$ if the nuclear kinetic energy is omitted from the Hamiltonian. Nevertheless, this proof is still of some interest for several reasons. First, no other method has yet been successfully extended to the case of completely dynamic nuclei; our proof indicates that the kinetic energy of the nuclei does not play a fundamental role, but merely presents a technical complication. Second, the proof closely follows physical intuition. Finally, it illustrates the important role that differences in threshold energy play in the analysis of molecular problems. Although this effect arose in our earlier work on positive molecular ions [12], we were unable to effectively estimate the threshold energy difference to obtain improved bounds in that case. It should be emphasized that our estimates are poor not because of the localization error arising from the nuclear kinetic energy, but because we break configuration space into many regions on each of which the effective potential is estimated rather crudely by a worst case approximation. The key to improved results using localization techniques is better potential theory for multi-center problems.

We now introduce some notation. Let \mathbf{R}_1 and \mathbf{R}_2 denote the positions of the two nuclei, $\xi_j (j=1 \dots N)$ the coordinates of the electrons, m and $M_k (k=1, 2)$ the electron and nuclear masses respectively, and $Z_k (k=1, 2)$ the nuclear charges. After removal of the center of mass motion, we choose as coordinates $\mathbf{R} \equiv \mathbf{R}_{12} = \mathbf{R}_1 - \mathbf{R}_2$ and $\mathbf{x}_i (i=1 \dots N)$ where $\mathbf{x}_j = \xi_j - \mathbf{R}_N$ is the position of the k -th electron relative to the nuclear center of mass $\mathbf{R}_N = \frac{M_1 \mathbf{R}_1 + M_2 \mathbf{R}_2}{M_1 + M_2}$. We also let $R = |\mathbf{R}_{12}|$ denote the internuclear distance, and

$$\xi_{j1} \equiv |\xi_j - \mathbf{R}_1| = \left| \mathbf{x}_j + \frac{M_2}{M_1 + M_2} \mathbf{R}_{12} \right|,$$

and

$$\xi_{j2} \equiv |\xi_j - \mathbf{R}_2| = \left| \mathbf{x}_j - \frac{M_1}{M_1 + M_2} \mathbf{R}_{12} \right|.$$

[Note that the definition of R used here differs from that in [12] by a factor of $(1 + \lambda)$.] The Hamiltonian relative to the center of mass can be

written as

$$\begin{aligned} H_{\text{CM}}(N, M_i, Z_i) = & \frac{M_1 + M_2}{2M_1 M_2} \Delta_{\mathbf{R}} - \frac{1}{2m} \sum_{i=1}^N \Delta_i \\ & + \frac{1}{2(M_1 + M_2)} \left| \sum_{i=1}^N \nabla_i \right|^2 + \sum_{i=1}^N \left(\frac{-Z_1}{\xi_{i1}} + \frac{-Z_2}{\xi_{i2}} \right) \\ & + \sum_{i < j} \frac{1}{|x_i - x_j|} + \frac{Z_1 Z_2}{R} \quad (1) \end{aligned}$$

where Δ_i denotes Δ_{x_i} , and $\left| \sum_{i=1}^N \nabla_i \right|^2$ is referred to as the Hughes-Eckart term. Recall that H acts on a suitable domain \mathcal{D} of smooth, square-integrable functions which are antisymmetric in the electron coordinates, (x_i, s_i) , where s_i denotes spin (which does not play an essential role in what follows). It will occasionally be useful to distinguish between the charge ratio $\omega = Z_1/Z_2$ and the mass ratio $\lambda = M_1/M_2$ (even though the assumption $M_k = Z_k M_0$ implies $\omega = \lambda$) and we always assume $\omega > 1$ and $\lambda > 1$, in particular, Z_1 *always denotes the larger charge*.

It follows from the limits on negative molecular ions that when the number of electrons N is large, the HVZ (Hunziker-van Winter-Zhislin) theorem ([3], [4]) reduces to

$$\begin{aligned} E_*[H_{\text{CM}}(N, M_i, Z_i)] \\ \equiv \inf \{ \sigma_{\text{ess}}[H_{\text{CM}}(N, M_i, Z_i)] \} = E_0[H_{\text{CM}}(N-1, M_i, Z_i)] \quad (2) \end{aligned}$$

where $\sigma[H]$ and $\sigma_{\text{ess}}[H]$ denote the spectrum and essential spectrum of the Hamiltonian H and $E_0[H]$ and $E_*[H]$ denote their respective infimums.

Section II contains a technical lemma needed to estimate the price of adding an electron to an already overcrowded nucleus, a description of some partitions of unity, and a few other useful facts. Section III contains the heart of the proof. Because this approach cannot yield optimal results in any case, we present a pedestrian argument which follows physical intuition, rather than trying to optimize each step. Section IV briefly discusses possible refinements, including an extension to bosonic systems.

II. PRELIMINARIES

A partition of unity is a set of functions $\{F_k\}$ such that $\sum_k F_k^2 = 1$. For a Hamiltonian H ,

$$\langle \Psi, H \Psi \rangle = \sum_k \langle F_k \Psi, (H - LE) F_k \Psi \rangle \quad (3)$$

and the localization error associated with such a partition is

$$LE = \sum_k F_k H F_k - H = \sum_{\mu} \sum_k c_{\mu} |\nabla_{\mu} F_k|^2 \tag{4}$$

where \sum_{μ} indicates a sum over all gradients for which a corresponding Laplacian (possibly including the Hughes-Eckart term) appears in the Hamiltonian, and c_{μ} denotes the corresponding coefficient.

Before stating our first result, we recall that the Hamiltonian for an atom with nuclear charge Z , nuclear mass M , and N electrons has the form

$$H_{at}(N, Z) = \sum_{i=1}^N -\frac{1}{2m} \Delta_i - \sum_{i=1}^N \frac{Z}{|x_i|} + \sum_{i < j} \frac{1}{|x_i - x_j|} + \frac{1}{2M} \left| \sum_{i=1}^N \nabla_i \right|^2 \tag{5}$$

where x_i denotes the position of the i -th electron relative to the nucleus. Let $N_{at}^c(Z)$ denote the maximum number of electrons an atom of charge Z can bind and $E_*(Z) = \inf_N E_*[H_{at}(N, Z)]$. Then

$$E_*(Z) = \inf_N E_0[H_{at}(N, Z)] = E_0[H_{at}(N_{at}^c(Z), Z)]. \tag{6}$$

Lieb [8] showed (for $M = \infty$) that $N_{at}^c(Z) \leq 2Z$; and others ([9], [11]) showed $\limsup_{Z \rightarrow \infty} \frac{N_{at}^c(Z)}{Z} = 1$. The following two additional observations about atomic systems will be useful in studying molecules.

LEMMA 1. — *If $N > 2(Z_1 + Z_2)$, there are positive constants σ and δ such that*

$$E_0[H_{at}(N, Z_1 + Z_2)] - E_0[H_{at}(N, Z_1)] \geq -\sigma N^{1/3} Z_1 Z_2 \geq -\delta (Z_1 + Z_2)^{1/3} Z_1 Z_2. \tag{7}$$

Proof. — The first inequality was established in [12] for arbitrary N (by a simple concavity argument). To establish the second, let $N^{\#} = N_{at}^c(Z_1 + Z_2)$ and note that

$$E_0[H_{at}(N, Z_1 + Z_2)] = E_0[H_{at}(N^{\#}, Z_1 + Z_2)]$$

and

$$E_0[H_{at}(N, Z_1)] \leq E_0[H_{at}(N^{\#}, Z_1)];$$

then apply the first inequality with $N = N^{\#} \leq 2(Z_1 + Z_2)$.

LEMMA 2. — *If $\text{supp } \Psi_A \subset \{x : |x| < A\}$, then*

$$\langle \Psi_A, H_{at}(N, Z) \Psi_A \rangle \geq E_*(Z) + \frac{M(M-1)}{4A(1+\gamma)} \tag{8}$$

where $N = M + N_0$, $N_0 = 2Z[1 + \gamma(Z)]$, $\lim_{Z \rightarrow \infty} \gamma(Z) = 0$ and $\gamma = \gamma(Z)$.

Proof. — Let $\varepsilon > 0$ be arbitrary, and let $\{J_k\}$ ($k = 0, \dots, N$) denote a partition of unity with the following properties:

(a) J_k ($k = 1, \dots, N$) is symmetric with respect to interchange of coordinates of particles in the set $\{1 \dots k - 1, k + 1 \dots N\}$; J_0 is symmetric in coordinates of all particles.

(b) $\text{supp } J_k \subset \{x : |x_i| < (1 + \varepsilon)|x_k| \forall i\}$ ($k = 1, \dots, N$);

(c) $\text{supp } J_0 \subset \{x : |x_i| < (1 + \varepsilon)\rho \forall i\}$ where ρ is a constant:

$$(d) \text{LE} = \sum_k |\nabla J_k|^2 < \begin{cases} \frac{C\sqrt{N}}{\rho^2} & \text{on } \text{supp } J_0 \\ \frac{C\sqrt{N}}{\rho|x_k|} & \text{on } \text{supp } J_k \end{cases} \quad \text{where } C \sim \varepsilon^{-2}. \quad (9)$$

The existence of such a partition follows from the work of Ruskai [5] and Sigal ([6], [7]) on non-existence of highly negative ions; for details see [7] and [14]. (Inclusion of the Hughes-Eckart term in (5) implies that \sqrt{N} should be replaced by $N^{(1/2)+(1/p)}$ in (9), but p can be arbitrarily large, so that $1/p \rightarrow 0$. Moreover, Simon ([7], [14]) has shown that \sqrt{N} can actually be replaced by N^σ where $\sigma > 0$ can be arbitrarily small.) Note that it follows immediately from (b) and (c) that

$$x \in \text{supp } F_k \Rightarrow |x_i - x_k| < (2 + \varepsilon)|x_k| \forall i \quad (k \neq 0). \quad (10)$$

The proof now proceeds by induction, *i. e.*, for $N > N_0$

$$\begin{aligned} \langle J_k \Psi_A, H_{\text{at}}(N, Z) J_k \Psi_A \rangle &\geq \langle J_k \Psi_A, H_{\text{at}}(N - 1, Z) J_k \Psi_A \rangle \\ &+ \int |J_k \Psi_A|^2 \frac{1}{|x_k|} \left(-Z + \frac{N - 1}{(2 + \varepsilon)} - \frac{C\sqrt{N}}{\rho} \right) \\ &\geq E_*(Z) \|J_k \Psi_A\|^2 + \frac{(M - 1)(M - 2)}{4A(1 + \gamma)} \|J_k \Psi_A\|^2 \\ &+ \int |J_k \Psi_A|^2 \frac{M - 1}{|x_k|(2 + \varepsilon)} + \int |J_k \Psi_A|^2 \frac{1}{|x_k|} \left(-Z + \frac{N - M}{(2 + \varepsilon)} - \frac{C\sqrt{N}}{\rho} \right) \\ &\geq E_*(Z) \|J_k \Psi_A\|^2 + \frac{M(M - 1)}{4A(1 + \gamma)} \|J_k \Psi_A\|^2 \end{aligned}$$

provided that $\varepsilon < \gamma$ and

$$\left(-Z + \frac{N - M}{(2 + \varepsilon)} - \frac{C\sqrt{N}}{\rho} \right) > 0. \quad (11)$$

Similarly, there is a constant $\sigma < 0$ such that

$$\begin{aligned} & \langle \Psi_A J_0, H_{at}(N, Z) \Psi_A J_0 \rangle \\ & \geq \left\{ -\sigma N^{1/3} Z^2 + \frac{(N-M)(N-1)}{4\rho} + \frac{M(N-1)}{4\rho} - \frac{C\sqrt{N}}{\rho^2} \right\} \|J_0 \Psi_A\|^2 \\ & > \frac{M(M-1)}{4A} \|J_0 \Psi_A\|^2 \end{aligned}$$

provided that

$$\left\{ -\sigma N^{1/3} Z^2 + \frac{(N-M)(N-1)}{4\rho} - \frac{C\sqrt{N}}{\rho^2} \right\} > 0. \quad (12)$$

It can be verified that there are positive constants a and β , such that (11) and (12) are satisfied if $N = M + 2Z(1 + \beta Z^{-1/18})$, $\rho^{-1} = \frac{4aN^{1/3}Z^2}{(N-M)(N-1)}$ and $\varepsilon = Z^{-1/18}$. When $M = 0, 1$ a similar argument holds without the induction step; therefore, the proof is complete.

We begin our analysis of molecular systems by defining a special type of cluster decomposition. Let $\alpha = (\alpha_1, \alpha_2)$ be a partition of $\{1 \dots N\}$ into two disjoint sets (one of which may be empty). The total system can be partitioned into two clusters corresponding to the first nucleus together with those electrons for which $i \in \alpha_1$ and the second nucleus together with those electrons for which $i \in \alpha_2$. The cluster Hamiltonian H_α is given by $H_\alpha = H_{CM} - I_\alpha$ where I_α is the intercluster potential

$$I_\alpha = - \sum_{i \in \alpha_1} \frac{Z_2}{\xi_{i2}} - \sum_{j \in \alpha_2} \frac{Z_1}{\xi_{j1}} + \sum_{i \in \alpha_1} \sum_{j \in \alpha_2} \frac{1}{|x_i - x_j|} + \frac{Z_1 Z_2}{R}. \quad (13)$$

By using the construction in [12] one can readily verify (*i. e.*, let $\omega = 1$ in eq. (20) of [12], even for $Z_1 \neq Z_2$) that there exists a partition of unity $\{G_\alpha\}$, indexed by cluster decompositions α , with the following properties:

(a) G_α is symmetric with respect to interchange of coordinates of particles within α_1 or α_2 ;

(b) $\text{supp } G_\alpha \subset \{x : \xi_{i1} < (1 + \varepsilon)\xi_{i2} \forall i \in \alpha_1 \text{ and } \xi_{i2} < (1 + \varepsilon)\xi_{i1} \forall i \in \alpha_2\}$ where $\varepsilon > 0$ is small;

(c) for H_{CM} given by (1), the localization error satisfies

$$LE \leq \frac{1}{\varepsilon^2 R^2} \left[NB_1 + \frac{N^2 B_2}{M_2} \right] \quad (14)$$

where M_2 denotes the *smaller* nuclear mass, and the constants B_k are independent of N, Z_k, M_k or R ; however, one expects to choose $\varepsilon \sim Z^{-s}$ for some $s > 0$.

Condition (b) implies that G_α localizes to a region in which electrons in a subcluster are bounded away from the opposite nucleus, *i. e.*, on $\text{supp } G_\alpha$,

$$i \in \alpha_k \Rightarrow \xi_{ik'} \geq R - \xi_{ik} \Rightarrow \xi_{ik'} \geq \frac{R}{2 + \varepsilon} \quad (k = 1, 2; k \neq k'). \quad (15)$$

The quadratic term in (14) arises from the nuclear kinetic energy; it was not evident in [12] because that paper only considered systems for which $Z_2 > N$ so that $\frac{N}{M_2} = \frac{N}{Z_2 M_0} < \frac{1}{M_0}$.

The functions $\{G_\alpha\}$ were constructed as products of one-particle functions defined in terms of a smooth, monotone function $g : \mathbf{R}^+ \rightarrow [0, 1]$ satisfying $g^2(t) + g^2(t^{-1}) = 1$ and $\text{supp } g \subset [(1 + \varepsilon)^{-1}, \infty]$, where $\varepsilon > 0$. Note that $g(t) = 0$ if $t < (1 + \varepsilon)^{-1}$, $g(t) = 1$ if $t > (1 + \varepsilon)$, $\text{supp } g'(t) \subset [(1 + \varepsilon)^{-1}, (1 + \varepsilon)]$ and $\text{sup } |g'(t)| = O(\varepsilon^{-1})$. Occasionally, we will write g_ε to emphasize a particular choice for ε .

The proof uses an additional partition defined in terms of a function $g = g_\varepsilon$ of the form described above by

$$F_1 = g\left(\frac{\mu R}{\|x\|_p}\right) g\left(\frac{\rho'}{R}\right); \quad F_2 = g\left(\frac{\mu R}{\|x\|_p}\right) g\left(\frac{R}{\rho'}\right); \quad (16a)$$

$$F_3 = g\left(\frac{\|x\|_p}{\mu R}\right) g\left(\frac{R}{\rho''}\right); \quad F_4 = g\left(\frac{\|x\|_p}{\mu R}\right) g\left(\frac{\rho''}{R}\right) \quad (16b)$$

where $\|x\|_p = \left(\sum_i |x_i|^p\right)^{1/p}$, $\mu = N^{1/p}(1 + \tilde{\varepsilon})$, ρ' and ρ'' are constants to

be chosen later, and we will eventually let $p \rightarrow \infty$. It is easy to verify that (with $p \geq 2$) the localization error arising from each F_k is bounded above by $\frac{\tilde{B}}{\tilde{\varepsilon}^2 r^2}$ where r denotes R , ρ' or ρ'' , as appropriate, and the constant \tilde{B}

is independent of N . Partitions of the form $\{G_\alpha\}$ and $\{J_k\}$ will subsequently be applied to F_2 and F_3 respectively. Because the localization errors from those partitions can grow like N^2 and \sqrt{N} respectively, $\tilde{\varepsilon}$ can be correspondingly smaller than ε without significantly affecting the bounds (9) and (14). Therefore, we will henceforth proceed as if the cutoffs in F_k are sharp in the sense that one can ignore $\tilde{\varepsilon}$ in

$$(1 + \tilde{\varepsilon})^{\pm 1} \approx (1 \pm \tilde{\varepsilon}) \approx 1;$$

this simplification will not affect the asymptotic estimates. It will also be useful to recall that (since $p > 1$)

$$|x_i| \leq \|x\|_\infty \leq \|x\|_p \leq N^{1/p} \|x\|_\infty \quad \forall i, \quad \text{and} \quad \lim_{p \rightarrow \infty} \|x\|_p = \|x\|_\infty. \quad (17)$$

III. PROOF

It follows from (3) and the variational principle that a Hamiltonian H has no discrete spectrum if one can find a partition of unity $\{F_k\}$ such that $\forall k$ and $\forall \Psi$ in $\mathcal{D}(H)$

$$\langle F_k \Psi, [H - L_k - E_*(H)] F_k \Psi \rangle \geq 0 \quad (18)$$

where L_k is the localization error on $\text{supp } F_k$. Our verification of (18) for $H = H_{\text{CM}}(N, M_i, Z_i)$ uses successive partitions of unity. It begins with the partition given by (16) for which F_3 and F_4 localize to regions in which outer electrons are far from both nuclei, in which case atomic techniques can be applied to an effective nuclear charge located at \mathbf{R}_N ; and for which F_1 and F_2 localize to regions in which all electrons are confined to a ball around both nuclei, in which case the techniques of [12] can be used. In both cases, control of the localization error requires that regions with relatively large (F_2 or F_3) and small (F_1 or F_4) internuclear distance be treated separately.

F_1 localizes to a region in which both nuclei and all electrons are very close together; *i. e.*, $\text{supp } F_1 \subset \{x : |x_i| < N^{1/p} \rho' \text{ and } R < \rho'\}$. Because H_{CM} is bounded below by the ground state energy of a "united atom" plus the nuclear repulsion [4], elementary arguments imply that

$$\begin{aligned} \langle F_1 \Psi, H_{\text{CM}} F_1 \Psi \rangle \\ \geq \left\{ -\sigma N^{1/3} Z_{\text{tot}}^2 + \frac{Z_1 Z_2}{\rho'} + \frac{N(N-1)}{4\rho'} \right\} \|F_1 \Psi\|^2. \end{aligned} \quad (19)$$

where $\sigma > 0$ and $Z_{\text{tot}} = Z_1 + Z_2$. However, the values of ρ' for which (19) is positive will lead to poor control of the localization error from $\{G_\alpha\}$, particularly when $Z_1 \gg Z_2$. To obtain a better bound, assume $N > 2Z_{\text{tot}}$ and apply Lemma 2 to the "united atom" Hamiltonian $H_{\text{at}}(N, Z_{\text{tot}})$ to conclude that

$$\begin{aligned} \langle F_1 \Psi, H_{\text{CM}} F_1 \Psi \rangle \\ \geq \left\{ E_0 [H_{\text{at}}(N, Z_{\text{tot}})] + \frac{1}{N^{1/p}} \frac{M(M-1)}{4(1+\gamma)\rho'} + \frac{Z_1 Z_2}{\rho'} \right\} \|F_1 \Psi\|^2 \end{aligned} \quad (20)$$

where M and γ are as in (8), *i. e.*, $M \approx (N - 2Z_{\text{tot}})$ and $\gamma \rightarrow 0$ as $Z_{\text{tot}} \rightarrow \infty$. Since (20) holds $\forall p$, one can eliminate the factor $N^{1/p}$ by taking $p \rightarrow \infty$. If this result is combined with $E_* [H_{\text{CM}}(N, M_i, Z_i)] \leq E_0 [H_{\text{at}}(N, Z_1)]$ and Lemma 1, one can conclude that

$$\begin{aligned} \langle F_1 \Psi, [H - L_1 - E_*(H)] F_1 \Psi \rangle \\ \geq \left\{ -\delta Z_{\text{tot}}^{1/3} Z_1 Z_2 + \frac{(N - 2Z_{\text{tot}})^2}{4\rho'} + \frac{Z_1 Z_2}{\rho'} - \frac{\tilde{B} \tilde{\epsilon}^{-2}}{(\rho')^2} \right\} \|F_1 \Psi\|^2, \end{aligned} \quad (21)$$

where γ has been ignored for simplicity. If N is sufficiently large, [assume $N > 4Z_{\text{tot}}$ so that $N - 2Z_{\text{tot}} > N/2$; for $Z_k \rightarrow \infty$, $N > 2Z_{\text{tot}}$ will do], one can find a constant $d > 0$ so that (21) is positive if

$$\frac{1}{\rho'} = d Z_{\text{tot}}^{1/3} Z_1 Z_2 N^{-2}. \quad (22)$$

In order to verify (18) on $\text{supp } F_2 = \{x : \|x\|_p < \mu R\}$, apply the partition of unity $\{G_\alpha\}$ to the function $\Psi_2 = F_2 \Psi$. It follows from the properties of $\{G_\alpha\}$, the fact that $\text{supp } \Psi_2 \subset \{x : |x_i| < N^{1/p} (1 + \tilde{\varepsilon})^2 R\}$, and Lemma 2, that there are constants a_k , and ζ_k such that $a_k \approx 1$, $\zeta_k \leq 2Z_k (1 + \gamma)$, and

$$\begin{aligned} & \langle G_\alpha \Psi_2, H_\alpha G_\alpha \Psi_2 \rangle \\ & \geq E_\alpha \|G_\alpha \Psi_2\|^2 + \frac{1}{N^{1/p}} \frac{\theta(N_1 - \zeta_1)^2}{4 a_1 R} + \frac{1}{N^{1/p}} \frac{\theta(N_2 - \zeta_2)^2}{4 a_2 R} \end{aligned} \quad (23)$$

where $\theta(t)^2 = \begin{cases} t^2 & \text{if } t > 0 \\ 0 & \text{if } t \leq 0 \end{cases}$; and the precise values of a_k depends on the mass ratio λ . It also follows from (15) that the intercluster repulsion I_α is bounded by

$$I_\alpha \geq -\frac{(2 + \varepsilon) N_1 Z_2}{R} - \frac{(2 + \varepsilon) N_2 Z_1}{R} + \frac{Z_1 Z_2}{R} + \frac{1}{N^{1/p}} \frac{N_1 N_2}{2 R} \quad (24)$$

where N_k denotes the numbers of electrons in α_k . Combining these results with $E_* \leq E_\alpha \equiv E_0(H_\alpha)$, one finds

$$\begin{aligned} & \langle G_\alpha \Psi_2, [H_{\text{CM}} - L_2 - E_*] G_\alpha \Psi_2 \rangle \\ & > \langle G_\alpha \Psi_2, [H_\alpha + I_\alpha - L_2 - E_\alpha] G_\alpha \Psi_2 \rangle \\ & > \frac{1}{R} \{Q_\alpha - \tilde{L}\} \|G_\alpha \Psi_2\|^2 \end{aligned} \quad (25)$$

where

$$Q_\alpha = \{ -(2 + \varepsilon) (N_2 Z_1 + N_1 Z_2) + Z_1 Z_2 + N^{-1/p} \Omega_{\lambda, \omega}(N_i) \}, \quad (26)$$

$$\Omega_{\lambda, \omega}(N_i) = \frac{N_1 N_2}{2} + \frac{\theta(N_1 - \zeta_1)^2}{4 a_1} + \frac{\theta(N_2 - \zeta_2)^2}{4 a_2}, \quad (27)$$

and \tilde{L} comes from the localization error. It follows from (14) and (22) that

$$\begin{aligned} \tilde{L} = R L_2 & > -\frac{\varepsilon^{-2}}{\rho'} \left[N B_1 + \frac{N^2 B_2}{M_2} \right] \\ & > -d \varepsilon^{-2} \left[\frac{B_1 Z_2}{N} + \frac{B_2}{M_0} \right] Z_{\text{tot}}^{1/3} Z_1 > -d \varepsilon^{-2} B Z_{\text{tot}}^{1/3} Z_1 \end{aligned} \quad (28)$$

where $B > 0$ is a constant and the second inequality used $M_2 \geq Z_2 M_0$. As above, the factor $N^{-1/p}$ can be eliminated. If ε is also ignored, one obtains

the asymptotic bound

$$Q_\alpha \geq -2(N_1 Z_2 + N_2 Z_1) + Z_1 Z_2 + \frac{N_1 N_2}{2} + \frac{\theta(N_1 - \zeta_1)^2}{4a_1} + \frac{\theta(N_2 - \zeta_2)^2}{4a_2}. \quad (30)$$

Although detailed analysis of (27) and (30) is messy, it is evident that $\Omega_{\lambda, \omega}$, and therefore Q_α , can be bounded below by an increasing quadratic function of N . By writing this function as $a(N - c Z_{\text{tot}})^2$, and letting $b = dB$, one can show that the right side of (25) satisfies

$$Q_\alpha - \tilde{L} > a(N - c Z_{\text{tot}})^2 - b \varepsilon^{-2} Z_{\text{tot}}^{1/3} Z_1 \quad (31)$$

It then follows that there is a constant η such that (31) is positive for $N > \eta(Z_1 + Z_2)$ and that in the limit $Z_{\text{tot}} \rightarrow \infty$, η is determined by (30). Before giving asymptotic bounds on η , we consider the rest of the partition.

It remains to consider the region in which at least one electron is bounded away from both nuclei, and observe that

$$|x_i| \geq R \Rightarrow -\frac{Z_1}{\xi_{i1}} - \frac{Z_2}{\xi_{i2}} > \frac{-2(Z_1 + Z_2)}{|x_i|}. \quad (32)$$

It follows from (17) that $\text{supp } F_3 \subset \{x : \|x\|_\infty \geq N^{1/p} R\}$ so that $\forall x \in \text{supp } F_3 \exists i$ such that the hypothesis of (32) holds. Therefore the techniques used on atomic problems can be applied using an effective nuclear charge of $Z_{\text{eff}} = 2(Z_1 + Z_2) = 2Z_{\text{tot}}$ in the difference $H_{\text{CM}}(N, M_i, Z_i) - H_{\text{CM}}(N - 1, M_i, Z_i)$. In particular, the proof of Lemma 2 can easily be modified to show that (18) holds for F_3 if $N > 2Z_{\text{eff}}[1 + \gamma(Z_{\text{eff}})]$. This procedure can be carried out with a partition of the form $\{J_k\} (k = 1, \dots, N)$, but excluding J_0 , the role of which is now played by F_4 . The asymptotic analogue of condition (11) is

$$-Z_{\text{eff}} + \frac{N - 1}{2} - \frac{C\sqrt{N}}{\rho''} > 0 \quad (33)$$

which one expects to hold asymptotically if $N > 2Z_{\text{eff}} = 4(Z_1 + Z_2)$. Control of the localization error is delicate because, unlike F_1 or J_0 , electrons are not confined on $\text{supp } F_4$; therefore, only the nuclear repulsion is available to control the localization error. Proceeding as before, one finds

$$\langle F_4 \Psi, [H - L_4 - E_*(H)] F_4 \Psi \rangle \geq \left\{ -\delta Z_{\text{tot}}^{1/3} Z_1 Z_2 + \frac{Z_1 Z_2}{\rho''} - \frac{\tilde{B} \tilde{\varepsilon}^{-2}}{[\rho'']^2} \right\} \|F_4 \Psi\|^2. \quad (34)$$

Now suppose that

$$Z_1 Z_2 > \kappa (Z_1 + Z_2)^{1/3} \quad (35)$$

where $\kappa = 4\delta\tilde{B}\tilde{\varepsilon}^{-2}$. Then one can again find a constant $d > 0$ so that (34) is positive for

$$\frac{1}{\rho''} = dZ_{\text{tot}}^{1/3}. \quad (36)$$

If this is inserted in (33) the result is positive for $N > 2Z_{\text{eff}}[1 + \gamma(Z_{\text{eff}})]$ where $\lim_{Z_{\text{eff}} \rightarrow \infty} \gamma(Z_{\text{eff}}) = 0$. However, the requirement (35) appears to restrict

the proof to systems in which at least one of the nuclear charges is large; in the case of homonuclear molecules, (35) becomes $Z > \kappa^{3/5}$. Conservative estimates suggest $100 < \kappa < 1,000$ so that this restriction, although not absurdly severe, would exclude such real molecules as O_2 (*i. e.*, oxygen). Fortunately, it is possible to substantially weaken this restriction when $Z_1 \approx Z_2$, and eliminate it entirely in the case of homonuclear molecules with realistic nuclear masses, by a more refined treatment of the localization error. The details, which are somewhat technical, are given in section IV. This completes the proof, with N^c bounded above by the maximum of the values required by the four different regions considered. With the estimates given thus far, the asymptotic bounds will be determined by the requirement that (30) be positive.

We now return to a more detailed analysis of that condition and first consider homonuclear molecules, *i. e.*, $\omega = \lambda = 1$ and $Z_1 = Z_2 = Z$. Then $a_k \leq \frac{\sqrt{5}}{2}[1 + O(\varepsilon)] \leq \frac{9}{2}$ for ε sufficiently small, so that

$$\Omega_{11} > \frac{1}{18}[9(n^2 - m^2) + 4\theta(n - \zeta + m)^2 + 4\theta(n - \zeta - m)^2] \quad (37)$$

where $N = 2n$ and $-n \leq m \leq n$. The minimum of (37) occurs when $m = \pm n$. Then using the estimate of $2Z$ for ζ , one finds that, asymptotically,

$$Q_\alpha > -2NZ + Z^2 + \frac{2}{9}(N - 2Z)^2$$

which is positive if $N > 12.4Z = 6.2(Z_{\text{tot}})$. As explained in section IV, by slightly decreasing μ this can be improved to $N > 5(Z_{\text{tot}})$.

When $M_1 \gg M_2$ the nuclei are not symmetrically located; one finds $a_k \approx 1 + 2\lambda^{-1} \approx 1$ where $\lambda = M_1/M_2$. In this case a better result is obtained if the right side of (30), rather than (27), is minimized. With m, n as above one has

$$Q_\alpha > -2nZ_{\text{tot}} + 2m(Z_1 - Z_2) + \frac{1}{4}[2n^2 - m^2] + \theta(n - \zeta_1 + m)^2 + \theta(n - \zeta_2 - m)^2]$$

which attains its minimum when $m = -n$; then if $\zeta_2 = 2Z_2$ one has the asymptotic bound

$$Q_\alpha > -2NZ_1 + \frac{1}{4}(N - 2Z_2)^2 + Z_1Z_2 > -2NZ_{\text{tot}} + \frac{1}{4}N^2$$

which is positive if $N > 8Z_{\text{tot}}$.

It may be amusing to observe that optimal estimates are obtained in the hypothetical case of a molecule (analogous to HD) for which $M_1 \gg M_2$ but $Z_1 = Z_2 = Z$. Then $a_k \approx 1$ and the bound above is minimal when $m = 0$ so that

$$Q_\alpha > -2NZ + \frac{N^2}{8} + \frac{1}{2}\left(\frac{N}{2} - 2Z\right)^2 + Z^2$$

which is positive if $N > 11Z > 5.5Z_{\text{tot}}$.

IV. REFINEMENTS AND EXTENSIONS

There is obviously considerable room for refinement of this proof; many of the approximations used have been rather crude. However, each of the refinements discussed here gives only a modest improvement in the bounds, often at the expense of considerable increase in technical complexity. A significant improvement requires a different approach. Our goal in presenting this proof is to establish that the nuclear kinetic energy does not have a significant effect on the number of electrons a molecule can bind. It should be emphasized that most of the localization error comes from the electron kinetic energy; if the nuclear masses are infinite, but the nuclei are not fixed [*i. e.*, the Hughes-Eckart and $\Delta_{\mathbf{R}}$ terms are removed from (1)] the proof is somewhat simpler, but the asymptotic results are not changed. In fact, when $M_k = \infty$, the quadratic terms disappear in (14); however, (34) is still problematic because of localization error from the kinetic energy of the electrons [see the discussion of (41) below]. Although the estimates given above compare unfavorably with Lieb's bound [8] of $N^c < 2(Z_1 + Z_2 + 1)$ for unconstrained nuclei (but without kinetic energy), this comparison also indicates that the poor bounds are a consequence of the method, rather than the inclusion of the nuclear kinetic energy. Unfortunately, less cumbersome proofs have not been able to accommodate nuclear kinetic energy.

It should be possible to considerably strengthen Lemma 2. Because $\limsup_{Z \rightarrow \infty} \frac{N_{\text{at}}^c(Z)}{Z} = 1$, one expects (8) to hold if $N_0 = Z[1 + \gamma(Z)]$. This would

imply $\zeta_k \approx Z_k$ in $\Omega_{\lambda, \omega}$; which would only improve the asymptotic bounds very slightly (to $Q_\alpha > 0$ if $N > 5Z_{\text{tot}}$ when $\lambda = \omega = 1$; but only negligibly, *i. e.*, $O(\omega^{-1})$ when $\lambda \approx \omega \gg 1$). However, improvement in another direction is also possible. The factor 4 in the denominator of (8) is equivalent to assuming that all the extra electrons lie on the surface of a ball of radius A , with each pair as far apart as possible. This is obviously not optimal. Although one expects the extra electrons to lie near the surface, they cannot all be a distance $2A$ apart. At the very least one ought to be able to replace 4 by 2 in this denominator. This would not only increase $\Omega_{\lambda, \omega}$ significantly, but also shift the minimizing configuration [from one in which most electrons are near one nucleus, to one in which the electrons are about evenly divided] so that all three terms in (27) make a substantial contribution to $\Omega_{\lambda, \omega}$. (For $\lambda \gg 1$ this would improve the condition $N > 8Z_{\text{tot}}$ to $N > 5.1Z_{\text{tot}}$). Although the effect of these improvements is modest, Lemma 2 is of sufficient independent interest to merit further investigation. Fefferman and Seco [11] have proved a similar result with $N_0 = Z(1 + \beta Z^{-s})$ but at the very severe price of multiplying the last term of (8) by Z^{-s} with $s > 0$, *i. e.* $4A \rightarrow Z^s A$ instead of the conjectured $4A \rightarrow 2A$.

As was discussed in [12], the requirement (18) is equivalent to

$$\langle G_\alpha \Psi_2, [H_\alpha + I_\alpha - L_\alpha - E_*] G_\alpha \Psi_2 \rangle > 0, \quad \forall \alpha. \quad (38)$$

However, because of the difficulty in estimating $(H_\alpha - E_*)$, we verified the stronger condition

$$\langle G_\alpha \Psi_2, [H_\alpha + I_\alpha - L_\alpha - E_\alpha] G_\alpha \Psi_2 \rangle > 0, \quad \forall \alpha. \quad (39)$$

The difference between these conditions, $(E_\alpha - E_*)$, represents the cost of moving electrons from one nucleus to another. Although we are still unable to estimate this threshold difference, Lemma 2 enabled us to estimate this cost another way. When the number of electrons is very large, or α has N_k reasonably balanced, this estimate is very good. However, when $N_k < N_{\text{at}}^c(Z_k)$, removing an electron from Z_k to the other nucleus raises the contribution that the corresponding atomic subsystem makes to $E_\alpha = E_0[H_{\text{at}}(N_1, Z_1)] + E_0[H_{\text{at}}(N_2, Z_2)]$. One expects this to make $E_\alpha \gg E_*$ whenever one $N_k \leq \zeta_k$. This should be sufficient to make $I_\alpha + (E_\alpha - E_*) > 0$. For configurations in which $E_\alpha \approx E_*$ one expects I_α (*i. e.* $N_1 N_2$) to be quadratic in N , even without the contribution from θ ; the additional quadratic terms involving θ estimate the cost of adding extra (*i. e.*, more than the individual atoms could accommodate separately) electrons to the system. If such an analysis could actually be implemented the result should be very good. However, the problem of obtaining analytic estimates on differences in threshold energies is notoriously difficult (*see, e. g.* [15], [16]).

Moreover, even if such estimates are obtained, they will not necessarily be in a form which readily permits comparison with I_α and L_α . Thus, although this discussion may give some insight into the nature of molecular problems, it is unlikely to lead directly to a better proof. Rather, it suggests that another procedure, which includes these ideas implicitly, is needed.

The treatment of F_3 mimics arguments which give an atomic estimate of $N_{\text{at}}^c(Z) \approx 2Z$ rather than $\approx Z$. If one of the atomic arguments for asymptotic neutrality ([9], [11]) could be modified so as to be applicable to $F_3 \Psi$, then the requirement $N > 2Z_{\text{eff}}$ arising from (25) could be replaced by $N > Z_{\text{eff}} = 2(Z_1 + Z_2)$. This is not completely straightforward because only can only use Z_{eff} in the difference between the N and $N-1$ electron Hamiltonians. One can also decrease the bounds obtained from F_3 by

modifying the choice of μ subject to the constraint $\mu > \frac{M_1}{M_1 + M_2} R$. Increasing

μ decreases Z_{eff} and thereby improves the bounds obtained from F_3 ; however, increasing μ also increases a_k which worsens the bounds obtained from F_2 . When λ is large, very small increases in μ yield substantial

decreases in Z_{eff} , [e. g., $\mu = (1 + \lambda^{-1})$ would give $Z_{\text{eff}} = \frac{3}{2}(Z_1 + Z_2)$] but

this cannot be exploited until the estimates involving F_2 are substantially improved. In the homonuclear case, one can improve (32) slightly so that

$Z_{\text{eff}} = 1.8(Z_1 + Z_2)$; if one then decreases μ until $Z_{\text{eff}} = \frac{5}{2}(Z_1 + Z_2)$, a_k is

sufficiently decreased to imply $Q_\alpha > 0$ if $N > 5Z_{\text{tot}}$, where this estimate includes the contribution from all four regions of the partition $\{F_k\}$.

We now indicate how one can weaken the restriction (35) by a more refined treatment of the localization error on $\text{supp } F_4$. A careful analysis shows that it can be decomposed into two parts. The first, which comes

from $\nabla_{\mathbf{R}}$, is proportional to $\frac{1}{M_2} = \frac{1}{Z_2 M_0}$; the second, which arises from

$\nabla_i g\left(\frac{\|x\|_p}{\mu R}\right)$, is nonzero only on a subregion (denoted by Γ_2) for which

$\|x\|_\infty \approx R$. Therefore, the electron repulsion can be used to control the second part. However, if we decompose H_{CM} and/or the domain of integration to exploit these observations, Lemma 1 cannot be used. Instead, one can extend known results for atomic systems to a Hamiltonian in which the electron repulsion is reduced by half. It thus follows that, if $N > 4Z_{\text{tot}}$,

$$H_{\text{at}}(N, Z_{\text{tot}}) - \frac{1}{2} \sum_{i < j} \frac{1}{|\mathbf{x}_i - \mathbf{x}_j|} > -\sigma Z_{\text{tot}}^{7/3} \quad (40)$$

where $\sigma > 0$ is a constant. If this observation is combined with bounds on the nuclear and electronic repulsion one finds

$$\begin{aligned} & \langle F_4 \Psi, [H - L_4 - E_*(H)] F_4 \Psi \rangle \\ & \geq \left\{ -\sigma Z_{\text{tot}}^{7/3} + \frac{Z_1 Z_2}{\rho''} - \frac{b_1 \tilde{\varepsilon}^{-2}}{Z_2 M_0 \rho''^2} \right\} \|F_4 \Psi\|^2 \\ & \quad + \int_{\Gamma_2} \left\{ \frac{N(N-1)}{8 \rho''} - \frac{b_2 \tilde{\varepsilon}^{-2}}{\rho''^2} \right\} |F_4 \Psi|^2 \quad (41) \end{aligned}$$

where b_k are constants and one has 8, rather than 4, in the denominator above because only half the electron repulsion is available. The other half was retained in $H_{\text{at}}(N, Z_{\text{tot}})$ so that the right side of (40) would be independent of N , *i. e.*, involve $Z_{\text{tot}}^{7/3}$ rather than $N^{1/3} Z_{\text{tot}}^2$. As before one can show that if

$$Z_1^2 Z_2^3 > \kappa' Z_{\text{tot}}^{7/3} \quad \text{where} \quad \kappa' = \sigma b_1 \tilde{\varepsilon}^{-2} M_0^{-1}, \quad (42)$$

then there is a constant $d \approx \sigma > 0$ so that the first term in (41) is positive when

$$\frac{1}{\rho''} = \frac{d Z_{\text{tot}}^{7/3}}{Z_1 Z_2}. \quad (43)$$

If this is inserted into the second term of (41) N can easily be made large enough to insure that both terms on the right side of (41) are positive. Moreover, for real nuclei $M_0 \approx 1,000 m$, which suggests that $\kappa' \approx 1$. Thus, in the case of homonuclear molecules, (42) reduces to $Z^{8/3} > \kappa \approx 1$, which is no restriction at all, and $\frac{1}{\rho''} = d Z_{\text{tot}}^{1/3}$ (where $d \approx \sigma$ is also modest) so that

(43) is similar to (36). However, (42) can never be satisfied when $Z_2 = 1$; and if $Z_1 \gg Z_2$, (42) is more restrictive than (35). Moreover, in these cases, (43) is less effective than (36) in controlling the localization error in (33).

If the “electrons” are bosons, then $N_{\text{at}}(N, Z)$ is bounded below by $-\sigma N Z^2$ rather than $-\sigma N^{1/3} Z^2$ and, correspondingly, the right side of (7) in Lemma 1 becomes $-\delta Z_{\text{tot}} Z_1 Z_2$. This leads to difficulties in controlling the localization error in both Lemma 2 and the main theorem because ρ , ρ' , and ρ'' must all be chosen correspondingly smaller. Thus, one must replace $N^{1/3}$ by N in (12), and $Z_{\text{tot}}^{1/3}$ by Z_{tot} in (21), (22), (34) and (36). Lemma 2 will still hold if $N_0 = c Z^{1+s}$, where c is a constant and $s > 0$ can be arbitrarily small. [This requires Simon’s observation [7], [14] that \sqrt{N} can be replaced by N^σ in (9) with $\sigma > 0$ arbitrarily small; a corresponding modification must also be made in (33).] Condition (35) must be replaced by $Z_1 Z_2 > \kappa (Z_1 + Z_2)$ and (42) by $Z_1^2 Z_2^3 > \kappa' (Z_1 + Z_2)^3$. In the case of homonuclear molecules the latter reduces, as before, to $Z^2 > \kappa' \approx 1$. For those values of Z_k which satisfy any of the above conditions, the theorem

holds with an asymptotic bound of $N^c \approx c(Z_1 + Z_2)^{1+s}$, where c is a constant and $s > 0$ can be arbitrarily small.

ADDENDUM

The fourth paragraph of Section IV describes a potential improvement dependent on extending $F_3\Psi$ one of the proofs of asymptotic neutrality of atoms. After this paper was accepted, the author received a manuscript [17] whose techniques appear adaptable to this purpose. The details will not be given here. However, it is worth also noting that Solovej [18] subsequently used this approach to establish that, if the Born-Oppenheimer approximation is used, the asymptotically neutrality of diatomic molecules can be proved. His argument requires a modification of the definition of stable bound state suitable for use in the Born-Oppenheimer approximation; the Hamiltonian must not only have a discrete eigenvalue, but must also satisfy $\inf_{\mathbf{R}} E(N, Z_i, \mathbf{R}) < E(N, Z_i, \mathbf{R} = \infty)$ where $E(N, Z_i, \mathbf{R})$ is the ground state energy of the fixed-nucleus Hamiltonian corresponding to the internuclear distance \mathbf{R} .

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(Manuscript received May 31, 1989)

(Accepted October 19, 1989.)