"Schrödinger inequalities" and asymptotic behavior of many-electron densities

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Upper bounds are derived to the many-electron density $\rho_k(x_1,\ldots,x_k)$ $(2 \le k \le n)$ of an n-electron atomic or molecular wave function. The derivation is based on former results on the decay of the one-electron density and on the "Schrödinger inequality" for $(\rho_k)^{1/2}$ which, by means of a comparison theorem, allows the deduction of upper bounds for ρ_k in the region $G^k = \{(x_1,\ldots,x_k) \,|\, r_i \ge c,\ 1 \le i \le k\}$, c being a constant and $r_i = |x_i|$, provided an upper bound to ρ_k is available on the boundary ∂G^k. The latter can be obtained from bounds to ρ_{k-1}. A recurrence procedure leads to the final result which for the case of an atom is given by $\rho_k \le dS\Pi_{i=1}^k r_i^{2[Z/2(2\epsilon_i)^{1/2}-1]} e^{-(2\epsilon_i)^{1/2} r_i}$ (d is a constant, S acts as a symmetrizer, Z denotes the nuclear charge, and the ϵ_i $(1 \le i \le k)$ denote the successive ionization potentials of the state under consideration). We further report an improved bound for ρ_2 which depends explicitly on the interelectronic distance.

I. INTRODUCTION

This paper generalizes results of a recent paper[1] (referred to as I) on asymptotic properties of one-electron densities of atoms and molecules to many-electron densities. We consider bound states of atomic and molecular systems described by a Hamiltonian in the infinite nuclear mass approximation

$$H = \sum_{i=1}^{n}\left(-\frac{\Delta_i}{2} - V(x_i)\right) + \sum_{i<j}^{n} |x_i - x_j|^{-1}, \tag{1.1}$$

$$V(x_i) = \sum_{j=1}^{m} |X_j - x_i|^{-1} Z_j, \tag{1.2}$$

and the corresponding eigenvalue problem

$$H\psi = E\psi, \tag{1.3}$$

where $\psi(x_1, \ldots, x_n)$ is the normalized wave function in configuration space R^{3n} (spin enters only via permutation symmetry). Our notation will follow essentially the notation of I.

Let us define the k-electron density by

$$\rho_k(x_1, \ldots, x_k) = \int |\psi(x_1, \ldots, x_n)|^2 dx_{k+1} \ldots dx_n. \tag{1.4}$$

We shall investigate the asymptotic properties of ρ_k for the case that all k electrons tend simultaneously to infinity.

This problem has been investigated so far only by Ahlrichs *et al.*[2] and by Hunziker *et al.*[3] for the many-particle case. For the three-particle problem the work of Slaggie and Wichmann,[4] Morgan,[5] and Mercuriev[6] should be mentioned. Other work[1,7-11] on the decay of subcontinuum wave functions deals only with the case that one particle (or one cluster in the general nonrelativistic many-particle problem) tends to infinity. The results obtained there contain only the first ionization potential ϵ_1 (for a definition of ϵ_1 see, for instance, I).

As has been shown for the three-particle problem[5] and for the many-particle problem[2,3] in certain regions of configuration space the other ionization potentials ϵ_i $(i > 1)$ [ϵ_i is defined as the first ionization potential of the $(i-1)$-fold ionized system derived from ψ] should also enter a more satisfactory description of the asymptotic behavior of a many-electron density. This can be easily visualized on physical grounds by considering an atom described by a Hamiltonian within the infinite nuclear mass approximation and without interelectronic repulsion. There the asymptotic behavior, aside from a polynomially bounded pre-exponential factor, is given by

$$\rho_k \propto S \exp\left(-\sum_{i=1}^{k} 2\sqrt{2\epsilon_i}\, r_i\right), \tag{1.5}$$

where S acts as a symmetrizer.

Here we shall obtain explicit upper bounds to ρ_k, for $r_1, \ldots, r_k$ greater than some constant c, which exhibit the same asymptotic behavior as (1.5) concerning the exponential factor (the existence of such bounds has been already conjectured by Morgan.[5]) For atomic two-electron densities we shall give an upper bound where the pre-exponential factor depends explicitly on the interelectronic distance. Although our results for the pre-exponential term are still not satisfactory, they improve the results reported previously by the present authors.[2] They seem to be also essentially in accordance, concerning the exponential factor, with the very general results of Hunziker *et al.* on the asymptotic behavior of subcontinuum wave functions.[3]

However, it should be noted that we, as every other worker in this field, obtain only upper bounds on the asymptotic behavior of ρ_k, whereas lower bounds remain a completely unsettled problem at least for Coulombic systems. (For three-particle systems with potentials decaying faster than the Coulomb potential, Mercuriev[6] obtained results on the exact asymptotic behavior.) For instance, it is not known whether or not the one-electron density of helium is decaying like, say $\exp(-r^2)$, which admittedly appears to be very unlikely on physical grounds, but has not been ruled out yet.

II. MATHEMATICAL PRELIMINARIES

Since subharmonic functions will frequently enter our subsequent considerations we recall their definition and some of their properties.

Let $B_r(x)$ denote the sphere $\{x' \in R^m : |x - x'| < r\}$ and let $S_r(x)$ and $|S_r(x)|$ denote the surface and surface area of $B_r(x)$, respectively. A function s, defined and continuous in a domain $D \subseteq R^m$ is called subharmonic (s.h.) if it satisfies the mean value inequality

$$s(x) \leq |S_r(x)|^{-1} \int_{S_r(x)} s(x')\, d\sigma(x'), \tag{2.1}$$

whenever $B_r(x) \subseteq D$. [$d\sigma(x)$ denotes the surface element of the sphere.]

It can be shown[13] that the following conditions are equivalent: (i) s is s.h.; (ii) $\Delta s \geq 0$ in the distribution sense. (If s has continuous second partial derivatives $\Delta s \geq 0$ in classical sense); and (iii)

$$s(x) \leq |B_r(x)|^{-1} \int_{B_r(x)} s(x')\, dx' \tag{2.2}$$

for every $B_r(x) \subseteq D$, $|B_r(x)|$ denotes the volume of $B_r(x)$. Furthermore it can be shown[14] that the mean value inequality (2.1) implies the maximum principle for s.h. functions. The maximum principle tells us that a nonconstant function s.h. in some domain D has its supremum at ∂D, the boundary of D.

A consequence of (2.2) is the following lemma which we shall apply frequently.

Lemma 1. Let $s: R^{mk} \to R$ be a non-negative, continuous integrable function s.h. in a domain $D \subseteq R^{mk}$ and let $(x_1, \ldots, x_k) \in D$ with $x_i \in R^m$ $(1 \leq i \leq k)$. Then for every $\delta > 0$ with $B_\delta^{(mk)}(x_1, \ldots, x_k) \subseteq D$

$$s(x_1, \ldots, x_k) \leq \frac{|B_\delta^{m(k-1)}|}{|B_\delta^{mk}|} \max_{(x_1', \ldots, x_{k-1}') \in B_\delta^{m(k-1)}(x_1, \ldots, x_{k-1})} \int_{R^m} s(x_1', \ldots, x_k')\, dx_k'. \tag{2.3}$$

Proof: Clearly $B_\delta^{(mk)}(x_1, \ldots, x_k) \subset B_\delta^{m(k-1)}(x_1, \ldots, x_{k-1}) \times R^m$ which together with (2.2) and the positivity of s leads to

$$s(x_1, \ldots, x_k) \leq |B_\delta^{(mk)}|^{-1} \int_{B_\delta^{m(k-1)}(x_1, \ldots, x_{k-1}) \times R^m} s(x_1', \ldots, x_k')\, dx_1' \cdots dx_k'. \tag{2.4}$$

Inequality (2.3) now follows immediately.

In Sec. III we shall derive upper bounds to the k-electron density with the aid of a slight modification of a comparison theorem given by Simon.[12]

Theorem 1. Let G be an unbounded domain in R^n with sufficiently smooth boundary ∂G. Suppose f and g are continuous functions in a neighborhood of $\overline{G}$ and that

(i) $\Delta|f| \leq V|f|$, $x \in G$,
(ii) $\Delta|g| \geq W|g|$, $x \in G$,
[(i) and (ii) are to be understood in the distributional sense]
(iii) $f, g \to 0$ as $|x| \to \infty$, $x \in G$,
(iv) $W(x) \geq V(x) \geq 0$, $x \in G$,
(v) $|f| \geq |g|$, $x \in \partial G$.
Then $|f| \geq |g|$, for all $x \in G$.

Proof. Let $\phi = |g| - |f|$ and $D = \{x \in G : \phi > 0\}$ which is open. (i) and (ii) together with (iv) lead to $\Delta\phi \geq 0$ for $x \in D$. Since $\phi \to 0$ for $x \in \partial D \cup \{\infty\}$ we conclude by the maximum principle that $\phi \leq 0$ on D. Therefore D is empty which proves our assertion.

III. SCHRÖDINGER INEQUALITIES AND ASYMPTOTIC BEHAVIOR OF THE MANY-ELECTRON DENSITY

In I we derived the following distributional inequalities for $\sqrt{\rho_k}$ $(1 \leq k \leq n)$ which we called Schrödinger inequalities because of their suggestive structure:

Theorem 2. Let ϵ_i $(i = 1, \ldots, k)$ be the successive ionization energies of a molecular or atomic system described by the Hamiltonian (1.1), then

$$\sum_{i=1}^{k} [-\tfrac{1}{2}\Delta_i + \epsilon_i - V(x_i)]\sqrt{\rho_k} + \sum_{i<j}^{k} |x_i - x_j|^{-1}\sqrt{\rho_k} \leq 0. \tag{3.1}$$

Especially for $k = n$, $\sum_{i=1}^{n} \epsilon_i = |E|$ and (3.1) reads $(H - E)|\psi| \leq 0$.

As for the one-electron density, (3.1) can be used to demonstrate the absence of local maxima of ρ_k in certain regions of configuration space. (3.1) implies that ρ_k is s.h. in every domain $D \subseteq \Omega^k$, $\Omega^k = \{(x_1, \ldots, x_k)$:

$$\sum_{i=1}^{k} [\epsilon_i - V(x_i)] + \sum_{i<j}^{k} |x_i - x_j|^{-1} > 0\}.$$

Hence by the maximum principle ρ_k has no local maxima for all $D \subseteq \Omega^k$.

For $k=1$, theorem 2 enabled us to derive an upper bound to $[\rho_1(x)]^{1/2}$ (Ref. 1), which we state here again for further reference.[15]

Theorem 3. Let $Z = \sum_{j=1}^m Z_j$, $p = \max_{1 \le j \le m} |X_j|$ and $r_0 \ge Z/\epsilon_1 + p$. Then

$$[\rho_1(x)]^{1/2} \le c r^{-1} W_{Z/\sqrt{2\epsilon_1}, 1/2}[2(r-p)\sqrt{2\epsilon_1}], \quad |x| = r \ge r_0, \quad (3.2)$$

where X_j are the nuclear positions.

$$c = v_0 r_0 [W_{Z/\sqrt{2\epsilon_1}, 1/2}(4Z/\sqrt{2\epsilon_1})]^{-1},$$

$$v_0 \ge \max_{|x|=r_0} [\rho_1(x)]^{1/2}, \quad (3.3)$$

and

$$W_{Z/\sqrt{2\epsilon_1}, 1/2}$$

denotes the Whittaker function.[16]

In the following we shall extend this result to the k-electron density ρ_k. To make the notation simpler we shall abbreviate

$$W_{Z/\sqrt{2\epsilon_j}, 1/2}[2(r_i - p)\sqrt{2\epsilon_j}]$$

by $W_j(r_i - p)$.

Theorem 4. Suppose $\epsilon_1 \le \epsilon_2 \ldots \le \epsilon_n$. Let $G_\delta = \{x \in R^3 : |x| \ge Z/\epsilon_1 + p + \delta\}$, $\delta > 0$, then there is a constant $a_\delta^{(k)}$ such that

$$[\rho_k(x_1, \ldots, x_k)]^{1/2} \le a_\delta^{(k)} \sum_{P \in S_k} \prod_{i=1}^{k} r_i^{-1} W_{P(i)}(r_i - p), \quad \text{for } (x_1, \ldots, x_k) \in G_\delta^k. \quad (3.4)$$

S_k denotes the symmetric group and G_δ^k is the k-fold Cartesian product of G_δ. The constant is given by

$$a_\delta^{(k)} = v_0 \left(\frac{Z}{\epsilon_1} + p\right) \left[W_1\left(\frac{Z}{\epsilon_1} + p\right)\right]^{-1} \left(\frac{Z}{\epsilon_1} + p + \delta\right)^{k-1} \times q \prod_{i=2}^{k} (c_\delta^{(i)})^{1/2} \left[W_i\left(\frac{Z}{\epsilon_1} + p + \delta\right)\right]^{-1}, \quad (3.5)$$

with

$$c_\delta^{(i)} = |B_\delta^{3(i-1)}| / |B_\delta^{(3i)}|, \quad (3.6)$$

$$q = \sup_{r \ge Z/\epsilon_1 + p + \delta} \{r(r-\delta)^{-1} W_1(r - p - \delta)[W_1(r-p)]^{-1}\}, \quad (3.7)$$

and v_0 as defined in (3.3). For $r_1, \ldots, r_k$ large enough, the asymptotic formula holds for some constant d:

$$[\rho_k(x_1, \ldots, x_k)]^{1/2} \le d \sum_{P \in S_k} \prod_{i=1}^{k} \{r_i^{-1}(r_i - p)^{Z/(2\epsilon_{P(i)})^{1/2}} \times \exp[-(2\epsilon_{P(i)})^{1/2}(r_i - p)]\}. \quad (3.8)$$

Remarks. (a) The assumption $\epsilon_1 \le \epsilon_2 \ldots$ appears natural on physical grounds. However, a proof of this conjecture is still lacking and seems to be a rather delicate problem since for a two-electron system in the infinite nuclear mass approximation the conjecture is easily verified, whereas it turns out to be false for a helium atom with finite nuclear mass and without interelectronic repulsion.
(b) The method we shall develop to prove Theorem 4 can also be used to verify Theorem 3 which has been proved in a different manner in I.

Proof. We first consider the case $k=2$ and proceed then by induction over k. For $k=2$ inequality (3.4) reads

$$[\rho_2(x_1, x_2)]^{1/2} \le a_\delta^{(2)} (r_1 r_2)^{-1} [W_1(r_1 - p) W_2(r_2 - p) + W_1(r_2 - p) W_2(r_1 - p)]. \quad (3.9)$$

Now let

$$f(x) = Z/(r-p), \quad (3.10)$$

Then obviously

$$0 \le \epsilon_i - f(x) \le \epsilon_i - V(x), \quad x \in G_\delta. \quad (3.11)$$

If we find a solution $v_2(x_1, x_2)$ of the differential equation

$$(-\tfrac{1}{2}\Delta_1 - \tfrac{1}{2}\Delta_2) v_2 + [\epsilon_1 + \epsilon_2 - f(x_1) - f(x_2)] v_2 = 0 \quad (3.12)$$

with the property

$$\sqrt{\rho_2} \le v_2 \quad \text{for } (x_1, x_2) \in \partial G_\delta^2, \quad (3.13)$$

(∂G_δ^2 denotes the boundary of G_δ^2), then Theorem 1 implies $\sqrt{\rho_2} \le v_2$ for $(x_1, x_2) \in G_\delta^2$ since $\sqrt{\rho_2}$ satisfies

$$(-\tfrac{1}{2}\Delta_1 - \tfrac{1}{2}\Delta_2)\sqrt{\rho_2} + [\epsilon_1 + \epsilon_2 - f(x_1) - f(x_2)]\sqrt{\rho_2} \le 0, \quad (3.14)$$

as can be seen from (3.1) and (3.11).

Obviously (3.12) can be factorized into differential equations like

$$-\tfrac{1}{2}\Delta u(r) + [\epsilon_j - f(r)] u(r) = 0, \quad (j = 1, 2). \quad (3.15)$$

Transformation of variables[17] leads to the differential equation for Whittaker functions with the solution $r^{-1}W_j(r-p)$. Therefore the function $\bar{v}_2$ given by

$$\bar{v}_2(x_1,x_2)=a_\delta^{(2)}(r_1r_2)^{-1}[W_1(r_1-p)W_2(r_2-p) + W_1(r_2-p)W_2(r_1-p)] \tag{3.16}$$

satisfies (3.12). We shall now show that this function satisfies (3.13). According to Lemma 1

$$[\rho_2(x_1,x_2)]^{1/2}\leqslant(c_{\delta'}^{(2)})^{1/2}\max_{|x-x_1|\leqslant\delta'}[\rho_1(x)]^{1/2},\quad 0<\delta'\leqslant\delta,\ (x_1,x_2)\in G_\delta^2 \tag{3.17}$$

Using Theorem 3 and the monotonicity of $W_1(r-p)r^{-1}$ for $r\geqslant Z/\epsilon_1+p$, (3.17) leads to

$$[\rho_2(x_1,x_2)]^{1/2}\leqslant(c_\delta^{(2)})^{1/2}v_0(Z/\epsilon_1+p)[W_1(Z/\epsilon_1)]^{-1}\times(r_1-\delta)^{-1}W_1(r_1-p-\delta). \tag{3.18}$$

For the next step of the proof we need the following lemma on Whittaker functions.

Lemma 2. Let t_0, ν be chosen such that $|\gamma|<t_0$ and $W_{\nu,1/2}(t)>0$ for $t\geqslant t_0-|\gamma|$, then there is a constant c_γ with

$$(t-\gamma)^{-1}W_{\nu,1/2}(t-\gamma)\leqslant c_\gamma t^{-1}W_{\nu,1/2}(t),\quad t\geqslant t_0. \tag{3.19}$$

Proof. For sufficiently large $t\geqslant t_1\geqslant t_0$ this follows by the asymptotic properties of the Whittaker functions[16]

$$W_{\nu,1/2}(t)=e^{-t/2}t^\nu[1+O(t^{-1})]. \tag{3.20}$$

For $t_0\leqslant t\leqslant t_1$ suppose (3.19) false. Then $W_{\nu,1/2}(t)>0$ leads to a contradiction to the boundedness of $W_{\nu,1/2}$ in this interval.

From (3.18) we can show after some manipulations with the aid of Lemma 2 that (3.9) holds for $(x_1,x_2)\in\partial G_\delta^2$. Now Theorem 1 implies that (3.9) holds for $(x_1,x_2)\in G_\delta^2$, hence proving Theorem 4 for $k=2$.

The extension to arbitrary k, $k\leqslant n$, is straightforward and will be done by induction over k. Therefore we assume that Theorem 4 holds for the case $k-1$.

Denoting the r.h.s. of (3.4) by $\bar{v}_k$ it can be shown in the same way as before that $\bar{v}_k$ is a solution of the differential equation

$$\sum_{i=1}^{k}[-\tfrac{1}{2}\Delta_i+\epsilon_i-f(x_i)]v_k=0, \tag{3.21}$$

with $f(x_i)$ defined according to (3.11). From (3.1) we see that

$$\sum_{i=1}^{k}[-\tfrac{1}{2}\Delta_i+\epsilon_i-f(x_i)]\sqrt{\rho_k}\leqslant0,\quad(x_1,\ldots,x_k)\in\partial G^k. \tag{3.22}$$

Hence in order to apply Theorem 1,

$$\sqrt{\rho_k}\leqslant\bar{v}_k,\ (x_1,\ldots,x_k)\in\partial G^k, \tag{3.23}$$

remains to be shown. Since this can be verified analogously to the case $k=2$ we just sketch the procedure: By Lemma 1 we have

$$[\rho_k(x_1,\ldots,x_k)]^{1/2}\leqslant(c^{(k)})^{1/2}\max_{(x_1',\ldots,x_{k-1}')\in B_\delta^{(k-1)}(x_1,\ldots,x_{k-1})}[\rho_{k-1}(x_1',\ldots,x_{k-1}')]^{1/2}. \tag{3.24}$$

Using the assumption that Theorem 4 holds for ρ_{k-1} we obtain (3.23) after some algebraic manipulations with the aid of Lemma 2. Application of Theorem 1 completes the proof of Theorem 4.

IV. CORRELATED BOUNDS FOR THE TWO-ELECTRON DENSITY OF ATOMIC SYSTEMS

The derivations presented in the preceding sections have been greatly simplified by the fact that the interelectronic repulsion could be neglected [cf. (3.1) with (3.12)]. However, proceeding this way we clearly could not derive the best possible bound for ρ_k obtainable from (3.1). Explicit inclusion of the interelectronic repulsion for ρ_2 leads—in complete analogy to the treatment in Sec. III—to the consideration of

$$(H^{(2)}+\epsilon_1+\epsilon_2)v(x_1,x_2)\geqslant0. \tag{4.1}$$

($H^{(2)}$ formally denotes the Hamiltonian of a two-electron atom) instead of (3.12) under the boundary condition (3.13), (4.1) is actually the Schrödinger equation of two-electron systems except for the different boundary condition. Since a complete solution appears hopeless we mainly tried to improve (3.9) in the neighborhood of $|x_1-x_2|=0$ and r_1,r_2 large since we expected in this region of configuration space a faster decay of the obtainable bound to ρ_2.

Our efforts in this direction have been only partly successful. Since the algebraic manipulations are tedious, though straightforward, we only sketch our considerations. The necessary derivations are conveniently performed using Hylleraas coordinates[18]

$$s=r_1+r_2,\ t=r_2-r_1,\ u=|x_1-x_2|,\ |t|\leqslant u\leqslant s. \tag{4.2}$$

Let

$$K=\tfrac{1}{2}(\sqrt{2\epsilon_1}+\sqrt{2\epsilon_2}),\quad k=\tfrac{1}{2}(\sqrt{2\epsilon_2}-\sqrt{2\epsilon_1}), \tag{4.3}$$

$$\gamma_i=Z/\sqrt{2\epsilon_i}-1,\quad i=1,2;\quad \gamma=\gamma_1+\gamma_2, \tag{4.4}$$

and let

$$\phi_{sp}(s,t)=\tfrac{1}{2}[(s-t)^{\gamma_1}(s+t)^{\gamma_2}e^{-kt}+(s-t)^{\gamma_2}(s+t)^{\gamma_1}e^{kt}]e^{-Ks}, \tag{4.5}$$

$$\phi_c(s,u)=s^{-\beta}s^{\gamma}e^{-Ks}e^{-ku}M(1+1/2k,2,2ku), \tag{4.6}$$

where M denotes the Kummer function.[16] Futhermore let

$$\phi=\min(\phi_{sp},\phi_c), \tag{4.7}$$

where ϕ_{sp} is just the asymptotically dominant term of the "Whittaker split-shell function" (3.9), and ϕ_c may be also written as

$$\phi_c(s,u)=\phi_{sp}(s,0)s^{-\beta}e^{-ku}M(1+1/2k,2,2ku). \tag{4.8}$$

We shall now prove the following refined asymptotic estimate for $\sqrt{\rho_2}$:

Theorem 5. If

$$k<\tfrac{1}{2} \tag{4.9}$$

and

$$0\leqslant\beta\leqslant\min\{2k^2Z/[K(K^2-k^2)],1/2k-1\} \tag{4.10}$$

then there is a constant $A(\beta)<\infty$, such that

$$\sqrt{\rho_2}\leqslant A\phi \tag{4.11}$$

for $(x_1,x_2)\in G$, $G=[(x_1,x_2):r_1,r_2\geqslant c]$.

Proof. We have to show that ϕ satisfies inequality (4.1) for $(x_1,x_2)\in G$ and that $A\phi$ satisfies the boundary conditions (3.13). We first get, after some algebra

$$(\phi_c)^{-1}(H^{(2)}+\epsilon_1+\epsilon_2)\phi_c\geqslant\frac{(K-Z)4s}{(s^2-t^2)}+\frac{2K(\gamma-\beta)}{s}+O(s^{-2}) \tag{4.12}$$

for $(x_1,x_2)\in G$. In (4.12) we took into account only the corresponding asymptotic terms since c can be chosen sufficiently large. If

$$\frac{(K-Z)4s^2}{(s^2-t^2)}+2K(\gamma-\beta)>0, \tag{4.13}$$

then (4.1) obviously holds. Let $\tilde{G}$ be the subset of G where (4.13) does not hold, i.e.,

$$(t/s)^2\geqslant 1-\frac{2(Z-K)}{[K(\gamma-\beta)]}. \tag{4.14}$$

The r.h.s. of (4.14) is positive by assumption (4.10). Hence, for c sufficiently large the use of the asymptotic expansion of M is justified in $\tilde{G}$, and it can be shown via (4.9) and (4.10) that

$$\phi_{sp}(s,t)\leqslant\phi_c(s,|t|)\ \text{in}\ \tilde{G}. \tag{4.15}$$

On the other hand,

$$\phi_c(s,|t|)\leqslant\phi_c(s,u)\ \text{in}\ \tilde{G} \tag{4.16}$$

since $\phi_c(s,u)$ is monotonically increasing in u and $|t|\leqslant u$. Hence we have $\phi=\phi_{sp}$ in $\tilde{G}$ and ϕ_{sp} clearly satisfies (4.1).

It remains to verify (4.12) for the points where ϕ_c equals ϕ_{sp}. Since $\phi=\frac{1}{2}(\phi_{sp}+\phi_c-|\phi_{sp}-\phi_c|)$ we conclude by Kato's inequality[19] that $\Delta\phi\leqslant\frac{1}{2}(\Delta\phi_{sp}+\Delta\phi_c)$ for $(x_1,x_2)\in G$ with $\phi_{sp}=\phi_c$. With this distributional inequality and the continuity of $\Delta\phi_{sp}$ and $\Delta\phi_c$ for these points it is not difficult to show that (4.1) holds.

As for the boundary conditions we first note that $A\phi_{sp}$ fulfills (3.13) for suitably chosen A because of (3.9). On ∂G we have $\phi=\phi_{sp}$—cf. (4.14)—except for a compact region near $r_1=r_2=c$ (where $\phi=\phi_c$) in which (3.13) clearly can also be satisfied for sufficiently large A.

Now let us compare the bound (4.11) for $\sqrt{\rho_2}$ with the one derived in Sec. III for the special case $u=0$. Inequality (3.8) then reads

$$\sqrt{\rho_2}\leqslant ds^{\gamma}e^{-Ks}, \tag{4.17}$$

whereas (4.11) yields

$$\sqrt{\rho_2}\leqslant As^{\gamma-\beta}e^{-Ks}. \tag{4.18}$$

This means we have improved the pre-exponential factor of the bound to $\sqrt{\rho_2}$ by $s^{-\beta}$ for $u=0$ under the presuppositions (4.9) and (4.10). However we do not know whether ρ_2 itself decays faster along $u=0$ compared, for instance, to the decay for $u=2r$, $t=0$, and $r\to\infty$. Our efforts to find functions satisfying (4.1) with stronger decay concerning the exponential factor failed. This supports our opinion that the interelectronic repulsion term in (4.1) affects only the pre-exponential factor in possible bounds.

The restriction (4.10) on β seems to be rather artificial and the condition (4.9) on k is certainly not satisfied for highly excited atoms. Nevertheless we note that the experimental ionization potentials and quantum-mechanical computations indicate that for ground states of neutral atoms with the exception of Li, Na, and possibly K, condition (4.9) is satisfied. In order to illustrate the restriction (4.10) imposed on β we briefly consider the ground state of He-like ions. The condition (4.9) holds for all $Z\geqslant 1$. By standard perturbation arguments we have

$$\epsilon_1=\tfrac{1}{2}Z^2-\tfrac{1}{8}5Z+O(1),\quad \epsilon_2=\tfrac{1}{2}Z^2, \tag{4.19}$$

which implies

$$\beta<\tfrac{25}{128}Z^{-2}+O(Z^{-3}) \tag{4.20}$$

[only for H^-, $Z=1$ is the second term in the minimum in (4.10) smaller than the first one]. Although we cannot say whether (4.20) is quantitatively or qualitatively significant, the trend $\beta \to 0$, if $Z \to \infty$ and hence $\phi \to \phi_{sp}$ appears reasonable. This is in accordance with perturbation theoretical considerations since in the $1/Z$-expansion the interelectronic repulsion enters with a Z^{-1} factor in the Hamiltonian.

Furthermore we point out that ϕ satisfies the so-called cusp condition[20] at the Coulomb singularity $u=0$:

$$\left.\frac{\partial \ln\phi}{\partial u}\right|_{u=0} = \left.\frac{\partial \ln\phi_c}{\partial u}\right|_{u=0} = \frac{1}{2}\,. \tag{4.21}$$

V. FINAL REMARKS

In order to discuss the quality and possible improvements of our bounds we have to consider the estimates we had to make. There are two estimates, both stemming from electronic repulsion terms, which affect the accuracy of our bounds in various ways: (i) In the derivation of the Schrödinger inequality (3.1) the most severe estimate is probably the neglect of the term

$$(n-k)(\sqrt{\rho_k})^{-1} \sum_{i=1}^{k} \int \frac{\rho_{k+1}(x_1,\ldots,x_{k+1})}{|x_i - x_{k+1}|}\, dx_{k+1}\,, \tag{5.1}$$

as can be seen following the derivation of the Schrödinger inequality in I. We expect that (5.1) behaves asymptotically for large r_i $(i=1,\ldots,k)$ like

$$(n-k)\sum_{i=1}^{k} r_i^{-1}\sqrt{\rho_k}\,. \tag{5.2}$$

Such a term would express the screening of nuclear charges seen by electrons at large distances from nuclei due to the presence of the remaining electrons. The effect of (5.2) if added on the l.h.s. of (3.1) would be the replacement of Z by a Z_{eff},

$$Z_{\text{eff}} = Z - (n-k)\,, \tag{5.3}$$

for r_i $(i=1,\ldots,k)$ large enough. This would change the pre-exponential term in the bound for $\sqrt{\rho_k}$ as already conjectured in I[21] for ρ_1. (ii) The other essential estimate in the derivation of the bound to $\sqrt{\rho_k}$ was the neglect of the term

$$\sum_{i<j}^{k} \frac{\sqrt{\rho_k}}{|x_i - x_j|} \tag{5.4}$$

in (3.1) in order to obtain a separable differential equation. By taking into account (5.4) we improved (Sec. IV) the bound (3.8) to $\sqrt{\rho_2}$ for the atomic case. The inclusion of this term accounts for the angular correlation of the bound. [(3.8) already shows in-out correlation.]

The estimates described in (i) and (ii) occur in each step of our recursion procedure for the bound to $\sqrt{\rho_k}$ and therefore the inaccuracy is propagated in each step. However, it seems reasonable to expect that the inclusion of the terms (5.1) and (5.4) does not affect the exponential factor of the bound (3.8). This conjecture is also supported by the fact that for $k=n$, i.e., $\sqrt{\rho_n} = |\psi|$, the right-hand side of (3.8) solves the Schrödinger equation asymptotically in those regions of configuration space where the potentials vanish.

Let us finally compare our present results with the results on asymptotic properties of electron densities obtained by the same authors in previous work[2] by completely different methods. There, upper bounds to expectation values have been derived which led also to an upper bound of a locally averaged k-electron density. This bound coincides essentially with (3.8) but is weaker concerning the pre-exponential factor and holds in a smaller part of configuration space.

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[15]Note that in (*I*) the right hand side of formulas (3.1) and (3.7) should read $cr^{-1}W_{Z/(2\epsilon)^{1/2},1/2}[2(r-p)(2\epsilon)^{1/2}]$.
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$$k r^{-1}(r-p)^{Z^*/\sqrt{2\epsilon}} e^{-\sqrt{2\epsilon}(r-p)}; \quad Z^* = Z - n + 1.$$