Bounds on the decay of electron densities with screening

Reinhart Ahlrichs
Institut für Physikalische Chemie, Universität Karlsruhe, Kaiserstrasse 12, 7500 Karlsruhe, Federal Republic of Germany

Maria Hoffmann-Ostenhof
Institut für Theoretische Physik, Universität Wien, Boltzmanngasse 5, 1090 Wien, Austria

Thomas Hoffmann-Ostenhof
Institut für Theoretische Chemie und Strahlenchemie, Universität Wien, Währingerstrasse 17, 1090 Wien, Austria

John D. Morgan III
Department of Physics, Princeton University, Princeton, New Jersey 08544
(Received 3 June 1980)

Differential inequality techniques are applied in the derivation of the following upper bound for the one-electron density $\rho(x)$ of atomic or molecular systems: $\sqrt{\rho(x)} \leq C(1+r)^{(Z-n+1)/\sqrt{2\epsilon}-1} e^{-\sqrt{2\epsilon}r}$ where $r=|x|$, ϵ is the first ionization potential, n the number of electrons, and Z the nuclear charge (or the sum of nuclear charges in the molecular case). Related bounds on the decay of the k-electron density and the wave function itself are also given. These bounds improve upon previous results [TH-O, MH-O, RA Phys. Rev. A **18**, 328 (1978)]. For the ground state of a two-electron atom (ion) we report a lower bound to $\rho(x)$ which exhibits the same functional form as the upper bound. Finally, for this case we give a lower bound to the wave function itself which shows essentially the same decay as the corresponding upper bound.

I. INTRODUCTION

In this article we generalize and improve upon the results of four recent articles,[1-4] (referred to as I, II, III, and IV, respectively), on asymptotic properties of k-electron densities $(k=1, \ldots, n)$ of atoms and molecules. Let us first define the notation. We consider arbitrary bound states of an n-electron atom with nuclear charge Z, described by the usual nonrelativistic Hamiltonian in the infinite nuclear mass approximation

$$H=\sum_{i=1,n}\left(-\frac{\Delta_i}{2}-\frac{Z}{r_i}\right)+\sum_{i<j}\frac{1}{r_{ij}},$$

$$x_i \in \mathbb{R}^3, \quad r_i=|x_i|, \quad r_{ij}=|x_i-x_j| \tag{1.1}$$

and the corresponding Schrödinger equation

$$(H-E)\psi(x_1, \ldots, x_n)=0, \tag{1.2}$$

where ψ is assumed to be real and normalized to unity. As is obvious from (1.1), (1.2) we consider "spinless" wave functions, as spin enters only in connection with the Pauli principle and permutational symmetry. The k-electron density is defined by

$$\rho_k(x_1, \ldots, x_k)=\int_{\mathbb{R}^{3(n-k)}}|\psi(x_1, \ldots, x_n)|^2 dx_{k+1}\cdots dx_n,$$

$$1 \leq k \leq n. \quad (1.3)$$

It should be noted that ρ_k as defined in (1.3) is not identical with the "physical" spinless k-electron density $\tilde{\rho}_k$ derived from an electronic wave function $\tilde{\psi}$ obeying the Pauli principle and including spin. $\tilde{\rho}_k$ is actually given by

$$\tilde{\rho}_k(x_1, \ldots, x_k)=\frac{1}{m}\sum_{\nu=1,m}\int_{\mathbb{R}^{3(n-k)}}|\psi_\nu(x_1, \ldots, x_n)|^2 dx_{k+1}\cdots dx_n,$$

where $\psi_\nu(\nu=1, \ldots, m)$ is the set of eigenfunctions belonging to the eigenvalue E (which is in general degenerate due to the permutational symmetry of H), from which the wave function $\tilde{\psi}$ is obtained by inclusion of spin. Since the differences between ρ_k and $\tilde{\rho}_k$ are immaterial for the following we shall work with ρ_k, which can be regarded as a "mathematical" k-particle density.

As the successive ionization potentials (I.P.'s) play a central role in the subsequent considerations let us recall their definition

$$\epsilon_1=E_0^{(n-1)}-E, \quad \epsilon_i=E_0^{(n-i)}-E_0^{(n-i+1)}, \tag{1.4}$$

where $E^{(n-j)}$, $1 \leq j \leq n$, denote the ground-state energies of the j-fold-ionized particle system described by the Hamiltonian

$$H^{(n-j)}=\sum_{l=j+1,n}\left(-\frac{\Delta_l}{2}-\frac{Z}{r_l}\right)+\sum_{l,m;\, j+1\leq l<m}\frac{1}{r_{lm}} \tag{1.5}$$

in the appropriate symmetry subspace as determined by the symmetry behavior of ψ, see I.

Henceforth we assume

$$\epsilon_1 \leq \epsilon_2 \leq \cdots \leq \epsilon_n . \tag{1.6}$$

A discussion of (1.6) is given in Sec. V. Let us now briefly review some results of I and II which are relevant to subsequent considerations.

Theorem 1.1. For a sufficiently large and C a suitable constant,

$$[\rho_k(x_1, \ldots, x_k)]^{1/2} \leq CS \prod_{i=1,k} r_i^{Z/\sqrt{2\epsilon_i}-1} e^{-\sqrt{2\epsilon_i} r_i}, \tag{1.7}$$

$$r_i \geq a, \quad 1 \leq i \leq k \leq n$$

where S acts as a symmetrizer. The derivation of Theorem 1.1 is based on the following differential inequality (to be understood in the distributional sense)

$$\left[\sum_{i=1,k}\left(-\frac{\Delta_i}{2} - \frac{Z}{r_i} + \epsilon_i\right) + \sum_{i<j;\, i,j=1,k} \frac{1}{r_{ij}}\right] \times [\rho_k(x_1, \ldots, x_k)]^{1/2} \leq 0 ,$$

$$1 \leq k \leq n, \tag{1.8}$$

which were called Schrödinger inequalities (I) because of their structure.

In I and II it was argued that the nuclear charge Z in the pre-exponential factor in (1.7) should be replaced by an effective charge $Z^* = Z - (n-k)$, at least. Our reasoning was based on the physically plausible picture that due to screening effects of the remaining $(n-k)$ electrons, the k electrons far from the nucleus "see" only an effective charge Z^*.

In this article, Sec. II contains some mathematical preliminaries and then in Sec. III upper bounds to ρ_k exhibiting the above-mentioned screening effects are derived. This will be achieved by an improvement in the Schrödinger inequalities (1.8). Moreover, the new bounds will hold in the entire configuration space, i.e., the condition $r_i \geq a$ on (1.7) can be dropped. For those regions of configuration space $\mathbb{R}^{3K}$ not covered in (1.7), the corresponding bounds are derived via Harnack-type inequalities (see Sec. II B). In addition we discuss for ρ_2 the effect of "electron correlation" [i.e., the effect of the $1/r_{ij}$ terms in the Schrödinger inequality (1.8)] on the asymptotic behavior.

In Sec. IV we improve a previously reported[3] lower bound on the ground state one-electron density of a two-electron atom, using a recently obtained lower bound to the corresponding wave function.[4] The new lower bound to ρ_1 has the same asymptotic behavior as the corresponding upper bound given in Sec. III. Using these results we then derive an improved lower bound to the ground-state wave function $\psi(x_1, x_2)$ which coincides in the exponential factors with the corresponding upper bound. In Sec. V we discuss these results in the context of some related open questions.

Remark 1.1. The restriction to the atomic case is done only for the sake of notational simplicity. All our results hold for molecules as well (in the clamped nucleus approximation) if Z is understood to stand for the sum of nuclear charges Z_ν, $Z = \sum_\nu Z_\nu$, in this case.

Remark 1.2. Since we are mainly interested in the asymptotic behavior the multiplicative constants occurring in the various bounds will be denoted by C even when they are different, provided that no confusion would result.

II. MATHEMATICAL PRELIMINARIES

A. Comparison theorems

Our derivations are largely based on the following two comparison theorems. Let Ω be an open subset of $\mathbb{R}^m$ and let f, g satisfy

(i) $f, g \in C^0(\bar{\Omega})$, $f \geq 0$ in Ω, and $f, g \xrightarrow{|x|\to\infty} 0$ if Ω is unbounded;

(ii) $g \leq f$, $\forall x \in \partial\Omega$, the boundary of Ω.

Theorem 2.1. (See II or Ref. 5.) Let f, g obey (i), (ii) and let further

(iii) $(-\Delta + W_1)g \leq 0$,
$(-\Delta + W_2)f \geq 0$,
in the weak sense in Ω;

(iv) $W_1 \geq W_2$ in Ω;

(v) $W_2 \geq 0$ in Ω.

Then $f \geq g$ in Ω.

Theorem 2.2. (See Ref. 6.) Let f, g obey (i) and (ii), and $f > 0$ almost everywhere in Ω. Let further

(iii) $(-\Delta + W_1)g \leq 0$,
$(-\Delta + W_2)f \geq 0$,
in the weak sense in Ω;

(iv) $W_1 > W_2$ almost everywhere in Ω; and

(v) $\Delta f, \Delta g \in L^1(\Omega)$.

Then $f \geq g$ in Ω.

Remark 2.1. For the reader's convenience we recall the meaning of certain symbols. $C^0(\bar{\Omega})$ denotes the class of functions which are continuous on the closure $\bar{\Omega}$ of Ω. A function φ is in $L^1(\Omega)$ if $\int_\Omega |\varphi| dx < \infty$. Theorem 2.1 is a simple consequence of the maximum principle. It has been used earlier[2,5] to study decay properties of subcontinuum wave functions. Theorem 2.2 has been proved for the one-dimensional case by Morgan[7] and for the general case by T. Hoffmann-Ostenhof,[6] who has also discussed some nontrivial applications. For subsequent considerations Theorem 2.1 would actually suffice. However, if Theorem 2.2 is used the condition $W_2 \geq 0$ need not be fulfilled, which facilitates applications.

B. Harnack–type inequalities

In order to bound ρ_k from above in those regions of configuration space where $r_i \geq a$ for all $i=1, \ldots, k$ does not hold we need the following estimate.

Theorem 2.3. Let $x=(x_1, \ldots, x_k) \in \mathbb{R}^{3K}$, and $u(x)$ a nonnegative continuous function with $\int_\Omega (u^2 + |\nabla u|^2) dx < \infty$, which satisfies $(-\Delta + W)u \leq 0$ in $\Omega \subset \mathbb{R}^{3k}$ in the distributional sense, where $W(x)$ is of "Coulombic type" (see Remark 2.2 below). Let $B_R(x_0)$ denote a $3k$-dimensional ball centered at x_0 with radius R, then

$$\sup_{x\in B_R(x_0)} u(x) \leq C\left(\int_{B_{2R}(x_0)} u^2(x) dx\right)^{1/2}; \tag{2.1}$$

for every ball $B_{2R} \subset \Omega$. The constant C depends on R and properties of W.

Remark 2.2. By "Coulombic" we mean

$$W(x_1, \ldots, x_k) = \sum_{l=1,k} V_l(r_l) + \sum_{i<j=1,k} V_{ij}(r_{ij}),$$

where $V_l(r)$, $V_{ij}(r)$ behave as $1/r$ for small r and remain finite for large r.

Theorem 2.3 is simply a special case of a class of general results on second-order elliptic partial differential equations and inequalities given by Trudinger;[8] see also the book by Gilbarg and Trudinger.[9] For the derivation of a lower bound to the ground state of two-electron atoms the following result will be essential.

Theorem 2.4 (weak Harnack inequality[8]). Let W and u be as in Theorem 2.3 and

$$(-\Delta + W)u = 0. \tag{2.2}$$

If $u \geq 0$ in $B_{4R}(x_0)$, then

$$\sup_{B_R(x_0)} u(x) \leq C \inf_{B_R(x_0)} u(x). \tag{2.3}$$

Remark 2.3. Theorem 2.4 is called a weak Harnack inequality since it is the natural extension of the well-known Harnack inequality in the theory of harmonic functions. We note that a number of related results have been obtained for quite general elliptic partial differential equations.[8] For further applications of the Harnack inequality to atomic and molecular physics see also Refs. 10 and 11. An immediate consequence of Theorem 2.4, which will be essential for Sec. IV is the following.

Corollary 2.1.[10-12] Mathematical ground-state wave functions (i.e., no Pauli principle imposed) of atoms and molecules are strictly positive, i.e. are bounded away from zero on compact sets. This follows from the well-known fact that ground states are positive almost everywhere,[13] together with Theorem 2.4. Wave functions are determined only up to an arbitrary phase, of course, and in Corollary 2.1 we have tacitly assumed a convenient choice of the phase, as usual in this context. Corollary 2.1 has recently been proved[10,11] in a different way in using Brownian motion arguments.

III. UPPER BOUNDS WITH SCREENING

We first state the main result as follows.

Theorem 3.1.

$$[\rho_1(x)]^{1/2} \leq C(1+r)^{(Z-n+1)/\sqrt{2\epsilon_1}-1} e^{-\sqrt{2\epsilon_1}\, r}, \quad \forall x \in \mathbb{R}^3 \tag{3.1}$$

$$[\rho_k(x_1, \ldots, x_k)]^{1/2} \leq CS \prod_{i=1,k} (1+r_i)^{(Z-n+k)/\sqrt{2\epsilon_i}-1} e^{-\sqrt{2\epsilon_i}\, r_i}, \tag{3.2}$$

$$\forall (x_1, \ldots, x_k) \in \mathbb{R}^{3k}, \quad 2 \leq k \leq n.$$

Remark 3.1. Let us briefly discuss the improvements achieved in (3.1) and (3.2) as compared to Theorem 1.1. Firstly, the bounds now hold in the entire configuration space whereas certain tubes—one or several electrons near the nucleus while the remaining ones tend to infinity—were excluded in Theorem 1.1. Secondly, the pre-exponential factors now include screening effects as discussed in the Introduction. The bound (3.1) for ρ_1 is optimal in this respect—as is further discussed in Sec. IV—whereas (3.2) includes screening only partially. This is especially obvious for $n=k$, where (3.2) yields the following bound for the wave function itself:

$$|\psi(x_1, \ldots, x_n)| = (\rho_n)^{1/2} \leq CS \prod_{i=1,n} (1+r_i)^{Z/\sqrt{2\epsilon_i}-1} e^{-\sqrt{2\epsilon_i}\, r_i}, \tag{3.2'}$$

which does not account explicitly for screening effects. This problem will be discussed further in connection with Theorem 3.2 which gives an improved bound for ρ_2.

Remark 3.2. As will be seen from the proof the constants C in (3.1), (3.2) could explicitly be evaluated (in principle) but this would be of little value since some quantities will have to be estimated rather crudely. The proof of Theorem 3.1 will be based on the following refinement of the Schrödinger inequalities (1.8).

Lemma 3.1.

$$\left(-\frac{\Delta_1}{2}+\epsilon_1-\frac{Z-n+1}{r_1}-\frac{d}{r_1^2}\right)[\rho(x_1)]^{1/2}\leqslant 0,\quad r_1\geqslant a \tag{3.3}$$

$$\left[\sum_{i=1,k}\left(-\frac{\Delta_i}{2}+\epsilon_i-\frac{Z-n+k}{r_i}-\frac{d}{r_i^2}\right)+\sum_{i<j}\frac{1}{r_{ij}}\right][\rho_k(x_1,\ldots,x_k)]^{1/2}\leqslant 0\,, \tag{3.4}$$

$$r_1,\ldots,r_k\geqslant a$$

for sufficiently large a and some positive constant d depending on Z, n, and k.

Proof of Lemma 3.1. To prove (3.3) we consider the operator

$$\bar{H}^{(n-1)}(x_1)=I^{(1)}\otimes H^{(n-1)}+\sum_{j=2,n}\frac{1}{r_{1j}}, \tag{3.5}$$

where $I^{(1)}$ is the identity operator on $L^2(\mathbb{R}^3,dx_1)$. Let $\bar{E}_0^{(n-1)}(x_1)$ denote the lowest eigenvalue of $\bar{H}^{(n-1)}(x_1)$ in the subspace $\mathcal{H}_{(\psi)}^{(n-1)}\subset L^2(\mathbb{R}^{3n-3},dx_2\cdots dx_n)$. Here $\mathcal{H}_{(\psi)}^{(n-1)}$ denotes the subspace which is induced by the symmetry behavior of ψ. $\bar{E}_0^{(n-1)}(x_1)$ depends parametrically upon x_1. The variational principle implies

$$\int\psi\bar{H}_{(x_1)}^{(n-1)}\psi\,dx_2\cdots dx_n\geqslant\bar{E}_0^{(n-1)}(x_1)\rho(x_1)\,. \tag{3.6}$$

By the Schrödinger equation itself and with the aid of a result derived in I,

$$-(\rho_1)^{1/2}\Delta_1(\rho_1)^{1/2}\leqslant-\int\psi\Delta_1\psi\,dx_2\cdots dx_n\,, \tag{3.7}$$

we arrive at

$$\left(-\frac{\Delta_1}{2}+\bar{E}_0^{(n-1)}(x_1)-E-\frac{Z}{r_1}\right)[\rho_1(x_1)]^{1/2}\leqslant 0\,. \tag{3.8}$$

From the results of Morgan and Simon[14] on the asymptotic behavior of Born-Oppenheimer molecular potential energy curves we know that $\bar{E}_0^{(n-1)}(x_1)$ has the asymptotic expansion

$$\bar{E}_0^{(n-1)}(x_1)=E_0^{(n-1)}+\frac{n-1}{r_1}+O\left(\frac{1}{r_1^2}\right). \tag{3.9}$$

Equation (3.9) is easily rationalized if the term $\sum_{j=2,n}1/r_{ij}$ occurring in (3.5) is treated by means of perturbation theory. Hence there is a constant d such that

$$\bar{E}_0^{(n-1)}(x_1)\geqslant E_0^{(n-1)}+\frac{n-1}{r_1}-\frac{d}{r_1^2}, \tag{3.10}$$

for r_1 sufficiently large. We should also mention that in Ref. 14 symmetry questions are discussed exhaustively and that the space $\mathcal{H}_{(\psi)}^{(n-1)}$ can be defined in a strict manner. However, we are only interested in the asymptotic behavior of $\bar{E}_0^{(n-1)}(x_1)$. Combining (3.8) with (3.10) and (1.4) inequality (3.3) results.

To prove (3.4) we proceed in an analogous manner; we have

$$\begin{aligned}\bar{E}_0^{(n-k)}(x_1,\ldots,x_k)&=\inf_{\|\varphi\|=1;\,\varphi\in\mathcal{H}_{(\psi)}^{(n-k)}}\int\varphi^*\left(I^{(k)}\otimes H^{(n-k)}+\sum_{i=1,k}\sum_{j=k+1,n}\frac{1}{r_{ij}}\right)\varphi\,dx_{k+1}\cdots dx_n\\&\geqslant\sum_{i=1,k}\inf_{\|\varphi\|=1;\,\varphi\in\mathcal{H}_{(\psi)}^{(n-k)}}\int\varphi^*\left(\frac{1}{k}I^{(k)}\otimes H^{(n-k)}+\sum_{j=k+1,n}\frac{1}{r_{ij}}\right)\varphi\,dx_{k+1}\cdots dx_n\,,\end{aligned} \tag{3.11}$$

where $I^{(k)}$ and $\mathcal{H}_{(\psi)}^{(n-k)}$ are defined by analogy with $I^{(1)}$ and $\mathcal{H}_{(\psi)}^{(n-1)}$. Equation (3.11) states that the infimum of the spectrum of a sum of operators does not exceed the sum of the infima of the spectra. For every summand on the right-hand side of (3.11) an asymptotic expansion corresponding to (3.9) can be used leading to (3.4).

Proof of Theorem 3.1. Let us first consider the one-electron density $\rho_1(x_1)$. We choose $\Omega=\{x_1\in\mathbb{R}^3: r_1\geqslant a\}$ in Theorem 2.1 with $\epsilon_1-(Z-n+1)/r_1-d/r_1^2>0$ for $r_1\geqslant a$. It is easily verified that the function

$$v_1(x_1)=Cr_1^{(Z-n+1)/\sqrt{2\epsilon_1}-1}(1-b/\sqrt{r_1})e^{-\sqrt{2\epsilon_1}\,r_1}\,, \tag{3.12}$$

with suitably chosen $b>0$, satisfies

$$-\frac{\Delta_1}{2}-\frac{Z-n+1}{r_1}+\epsilon_1-\frac{d}{r_1^2}\,v_1(x_1)\geqslant 0\,, \tag{3.13}$$

for $r_1\geqslant a$, a sufficiently large. Since $\rho_1(x_1)$ obeys (3.3) and condition (i) of Theorem 2.1, we can apply Theorem 2.1. Thus, if we choose the constant C large enough so that for $|x_i|=a$,

$$v_1(x_1)\geqslant\max_{|x_1|=a}[\rho_1(x_1)]^{1/2}\,, \tag{3.14}$$

then $v_1(x_1)\geqslant[\rho_1(x_1)]^{1/2}\;\forall r_1\geqslant a$ follows. Since the $b/\sqrt{r_1}$ can be absorbed into the constant C, inequality (3.1) holds for $r_1\geqslant a$. For $r_1\leqslant a$, (3.1) is fulfilled with suitably chosen C since $\rho_1(x_1)$ is bounded. It should be mentioned that a Whittaker function[15] solves Eq. (3.13) showing the same asymptotic behavior as (3.12).

For the proof of (3.2) we proceed in analogy with the method given in II. We therefore indicate only the main steps of the proof for the two-electron density $\rho_2(x_1,x_2)$. The result for ρ_k and $|\psi|$ itself is then obtained by a recursive procedure.

Let $\Omega=\{(x_1,x_2)\in\mathbb{R}^6\colon r_1,r_2\geq a\}$ with a sufficiently large so that (a)

$$\epsilon_1+\epsilon_2-\sum_{i=1,2}[(Z-n+2)/r_i+d/r_i^2]\geq 0\,,$$

and (b) Eq. (3.4) holds in Ω. Neglect of the positive interelectronic repulsion term yields

$$\left[-\frac{\Delta_1}{2}-\frac{\Delta_2}{2}+\epsilon_1+\epsilon_2-(Z-n+2)\left(\frac{1}{r_1}+\frac{1}{r_2}\right)\right](\rho_2)^{1/2}\leq 0,\quad \forall(x_1,x_2)\in\Omega\,. \tag{3.15}$$

Furthermore $(\rho_2)^{1/2}$ obeys condition (i) of Theorem 2.1. If we can find a function $v_2(x_1,x_2)>0$ satisfying (i) (3.15) in the other direction and (ii) $v_2(x_1,x_2)\geq[\rho_2(x_1,x_2)]^{1/2}$ on $\partial\Omega$, then by Theorem 2.1 v_2 is an upper bound to $\sqrt{\rho_2}$ in Ω. A straightforward computation shows that (i) holds for

$$v_2(x_1,x_2)=CS\prod_{i=1,2}r_i^{(Z-n+2)/\sqrt{2\epsilon_i}-1}\left(1-\frac{b}{\sqrt{r_i}}\right)e^{-\sqrt{2\epsilon_i}\,r_i}\,. \tag{3.16}$$

In order to verify (ii) we need the following.

Lemma 3.2.

$$\rho_2(x_1,x_2)\leq C_\delta\max_{x_1'\in B_\delta(x_1)}\rho_1(x_1')\quad \delta>0;\ \ x_1,x_2\in\mathbb{R}^3\,, \tag{3.17}$$

where $B_\delta(x_1)$ denotes a ball with radius δ in $\mathbb{R}^3$ centered at x_1.

Proof. Since (1.8) holds in $\mathbb{R}^6$ for $\sqrt{\rho_2}$ and

$$\int\{\rho_2(x_1,x_2)+|\nabla[\rho_2(x_1,x_2)]^{1/2}|^2\}dx_1\,dx_2\leq 1+\int|\nabla\psi|^2dx_1\cdots dx_n<\infty$$

(due to Lemma 2 in I), Theorem 2.3 implies

$$[\rho_2(x_1,x_2)]^{1/2}\leq C_\delta\left(\int_{B_\delta(x_1,x_2)}\rho_2(x_1',x_2')dx_1'\,dx_2'\right)^{1/2}\leq C_\delta\left(\int_{B_\delta(x_1)}\rho_1(x_1')dx_1'\right)^{1/2}\leq C_\delta\left[\max_{x_1'\in B_\delta(x_1)}\rho_1(x_1')\right]^{1/2}. \tag{3.18}$$

Remark 3.3. This estimate is a generalization of an analogous estimate in II, where (3.17) was shown for regions where $\sqrt{\rho_2}$ is subharmonic. Now the bound (3.1) to $\rho_1(x_1)$ can be used to obtain a bound for

$$\rho_2(x_1,x_2)\ \text{ on }\partial\Omega=\{(x_1,x_2)\in\mathbb{R}^6\colon r_1\geq a,r_2=a\}\cup\{(x_1,x_2)\in\mathbb{R}^6\colon r_1=a,r_2\geq a\}\,.$$

Choosing the constant C in (3.16) large enough leads to $v(x_1,x_2)\geq[\rho_2(x_1,x_2)]^{1/2}$ on $\partial\Omega$, hence proving (ii). By Theorem 2.1 inequality 3.2 for ρ_2 holds in Ω. To extend this result to all of $\mathbb{R}^6$ we proceed as above: Since the differential inequality (1.8) holds for $\sqrt{\rho_2}$ in $\mathbb{R}^6$ we can apply Theorem 2.3 in the region

$$\{(x_1,x_2)\colon r_1\geq a,r_2\leq a\}\cup\{(x_1,x_2)\colon r_1\leq a,r_2\geq a\}$$

to extend our bound into these tubes keeping the boundedness of ρ_2 in mind. This proves (3.2) for $k=2$.

Remark 3.4. Our upper bound to $\sqrt{\rho_2}$ is still not entirely satisfactory since it is easily seen that we have lost information. Namely, the bound (3.16) for fixed x_2 behaves asymptotically as

$$(1+r_1)^{(Z-n+2)/\sqrt{2\epsilon_1}-1}\,e^{-\sqrt{2\epsilon_1}r_1}\,.$$

Whereas we know from (3.17) that the pre-exponential factor should rather be $(1+r_1)^{(Z-n+1)/\sqrt{2\epsilon_1}-1}$. By taking into account the hitherto neglected $1/r_{12}$ term in (3.15), we obtain the following improved upper bound.

Theorem 3.2.

$$[\rho_2(x_1,x_2)]^{1/2}\leq CS[(1+r_1)^{\alpha-1}(1+r_2)^{\beta-1}e^{-\sqrt{2\epsilon_1}\,r_1-\sqrt{2\epsilon_2}\,r_2}]\,,\quad \forall(x_1,x_2)\in\mathbb{R}^6 \tag{3.19}$$

where

$$\alpha=(Z-n+1)/\sqrt{2\epsilon_1}$$

and

$$\beta>(Z-n+\tfrac{5}{2})/\sqrt{2\epsilon_2}\,.$$

The proof is a rather tedious application of Theorem 2.1 and will be sketched in Appendix A.

We note that (3.19) shows two different screening effects. The constant α determines the pre-exponential term for the outer electron and it includes full screening of Z by the remaining $(n-1)$ electrons. For β, which refers to the "inner" electron, we could expect at best (if the outer electron tends faster to infinity than the inner one) $\beta \approx (Z-n+2)/\sqrt{2\epsilon_2}$. However, if $x_1=-x_2$, $r_1=r_2=r\to\infty$, the electrons "feel" a potential $-2(Z-n+2-\frac{1}{4})/r$, corresponding to an effective charge $Z^*=Z-n+\frac{7}{4}$, which is just the average of the numerators in the expressions for α and β. Although this is a vague intuitive reasoning only, it could be considered as an indication that β as given in (3.19) cannot be improved, at least if $\epsilon_1\approx\epsilon_2$, i.e. if $Z\to\infty$.

Finally we note that we attempted to improve (3.19) by considering upper bounds with an explicit r_{12} dependence. Again using Theorem 2.1., we obtained an upper bound to ρ_2 which shows angular correlation and which behaves for $r_{12}=0$ like

$$Fr_1^{-\gamma},\gamma<\min[(\sqrt{2\epsilon_2}-\sqrt{2\epsilon_1})^{-1},1], \tag{3.20}$$

where F denotes the rhs of (3.19). It turns out to be extremely difficult to exhaust the differential inequality for $\sqrt{\rho_2}$ with respect to the r_{12} dependence of the upper bound, and we do not attach much physical significance to (3.20).

IV. LOWER BOUNDS

In the following we consider the mathematical ground state (singlet S state) of a two-electron atom. By corollary 2.1, $\psi(x_1,x_2)>0$ for $r_1,r_2<\infty$. We have the following lower bound to $\sqrt{\rho_1}$.

Theorem 4.1.

$$[\rho_1(x_1)]^{1/2}\geq C(1+r_1)^{(Z-1)/\sqrt{2\epsilon_1}-1}e^{-\sqrt{2\epsilon_1}r_1},\quad \forall x_1\in\mathbb{R}^3. \tag{4.1}$$

Remark 4.1. Except for the multiplicative constant the lower bound shows exactly the same asymptotic behavior as the upper bound (3.1). We have therefore the following corollary.

Corollary 4.1. There are two positive constants $0<C_-<C_+<\infty$ such that

$$C_-(1+r_1)^{(Z-1)/\sqrt{2\epsilon_1}-1}e^{-\sqrt{2\epsilon_1}r_1}\leq[\rho_1(x_1)]^{1/2}\leq C_+(1+r_1)^{(Z-1)/\sqrt{2\epsilon_1}-1}e^{-\sqrt{2\epsilon_1}r_1} \tag{4.2}$$

The proof of Theorem 4.1 relies heavily on the following nonisotropic lower bound to ψ which was obtained in IV.

Theorem 4.2. For every $\delta>0$ there exists a constant $C_\delta>0$ so that

$$\psi(x_1,x_2)\geq C_\delta(e^{-(\sqrt{2\epsilon_1}+\delta)r_1-\sqrt{2\epsilon_2}r_2}+e^{-(\sqrt{2\epsilon_1}+\delta)r_2-\sqrt{2\epsilon_2}r_1}),\quad \forall(x_1,x_2)\in\mathbb{R}^6. \tag{4.3}$$

Remark 4.2. This result was derived using the lower bound to $\sqrt{\rho_1}$ given in III by means of Theorem 2.4 and a comparison argument. For a related procedure see the proof of Theorem 4.3 below.

Remark 4.3. To our knowledge, there exist so far only a few results on lower bounds to ground states,[16-19] none of which deal with the Coulombic case.

Proof of Theorem 4.1. The proof is patterned somewhat after the considerations given in III. Let $\phi(x_2)$ be the ground state of the corresponding ionized system, satisfying

$$\left(-\frac{\Delta_2}{2}-\frac{Z}{r_2}\right)\phi(x_2)=-\frac{Z^2}{2}\phi(x_2) \tag{4.4}$$

and let

$$u(x_1)=\int\psi(x_1,x_2)\phi(x_2)\,dx_2. \tag{4.5}$$

By Corollary 2.1, $u>0$. The symmetry properties of ψ and ϕ imply that u is spherically symmetric. Furthermore, from the Cauchy-Schwarz inequality,

$$u(x_1)\leq[\rho_1(x_1)]^{1/2}. \tag{4.6}$$

By considering the expression

$$\int\phi(x_2)(H-E)\psi(x_1,x_2)\,dx_2$$

we obtain

$$\left(-\frac{\Delta_1}{2}-\frac{Z}{r_1}+\epsilon_1\right)u(x_1)+\int\psi(x_1,x_2)\phi(x_2)|x_1-x_2|^{-1}dx_2=0. \tag{4.7}$$

To prove (4.1) we have to find a good upper bound to $\int\psi\phi|x_1-x_2|^{-1}dx_2$, which will enable us to use a comparison theorem on the resulting differential inequality. We start with the following inequality,

$$\int\frac{\psi(x_1,x_2)\phi(x_2)}{|x_1-x_2|}dx_2=\int_{r_2<r_1/2}+\int_{r_2\geq r_1/2}\leq\frac{2u(x_1)}{r_1}+[\rho_1(x_1)]^{1/2}\left(\int_{r_2\geq r_1/2}\phi^2|x_1-x_2|^{-2}dx_2\right)^{1/2}, \tag{4.8}$$

where we used the Cauchy-Schwarz inequality. Now the upper bound to $\sqrt{\rho_1}$ (3.1), together with an L^∞ estimate using the explicit form of $\phi(x_2)$ leads to

$$\int\frac{\phi(x_2)\psi(x_1,x_2)}{|x_1-x_2|}dx_2\leq\frac{2u(x_1)}{r_1}+C(1+r_1)^{(Z-1)/\sqrt{2\epsilon_1}-1}e^{-\sqrt{2\epsilon_1}r_1-Zr_1/4}\left(\int\phi|x_1-x_2|^{-2}dx_2\right)^{1/2}. \tag{4.9}$$

However, the lower bound to ψ (4.3) implies that for every $\delta>0$ there is a $K_\delta>0$, so that

$$u(x_1)\geq K_\delta e^{-(\sqrt{2\epsilon_1}+\delta)r_1}. \tag{4.10}$$

Hence, noting $\int\phi|x_1-x_2|^{-2}dx_2<\infty$ for $r_1>b>0$, and choosing $\delta<Z/4$, we obtain for some positive constants C,α

$$\int\frac{\phi(x_2)\psi(x_1,x_2)}{|x_1-x_2|}dx_2\leq\frac{2u(x_1)}{r_1}+Ce^{-\alpha r_1}u(x_1),\quad r_1>b \tag{4.11}$$

which leads to

$$\left(-\frac{\Delta_1}{2}-\frac{(Z-2)}{r_1}+Ce^{-\alpha r_1}+\epsilon_1\right)u(x_1)\geq 0. \tag{4.12}$$

We easily find a function v such that

$$\left(-\frac{\Delta_1}{2}-\frac{(Z-2)}{r_1}+Ce^{-\alpha r_1}+\epsilon_1\right)v(x_1)\leq 0\quad\text{for } r_1>b, \tag{4.13}$$

with $v(b)\leq u(b)$, which behaves asymptotically as $(1+r_1)^\beta e^{-\sqrt{2\epsilon_1}r_1}$ for some finite constant β. Therefore, comparison Theorem 2.1 implies that

$$u(x_1)\geq A(1+r_1)^\beta e^{-\sqrt{2\epsilon_1}r_1}, \tag{4.14}$$

with A a suitable constant.

Using (4.14), we estimate $\int\phi\psi|x_1-x_2|^{-1}dx_2$ again:

$$\int\frac{\phi(x_2)\Psi(x_1,x_2)}{|x_1-x_2|}dx_2=\int_{r_2<\sqrt{r_1}}+\int_{r_2\geq\sqrt{r_1}}\leq\frac{u(x_1)}{r_1-\sqrt{r_1}}+[\rho_1(x_1)]^{1/2}\left(\int_{r_2\geq\sqrt{r_1}}\phi^2(x_2)|x_1-x_2|^{-2}dx_2\right)^{1/2}. \tag{4.15}$$

We proceed now in a completely analogous fashion to the previous estimates but using (4.14) instead of (4.10) and obtain the following differential inequality for u:

$$\left(-\frac{\Delta_1}{2}-\frac{Z-1}{r_1}+\epsilon_1+Ke^{-\gamma\sqrt{r_1}}+K'r_1^{-3/2}\right)u(x_1)\geq 0 \tag{4.16}$$

for some positive constants K, K', and γ. By the same reasoning which led from (4.12) to (4.14) we obtain

$$u(x_1)\geq C(1+r_1)^{(Z-1)/\sqrt{2\epsilon_1}-1}e^{-\sqrt{2\epsilon_1}r_1}. \tag{4.17}$$

By (4.6), this is also a lower bound to $\sqrt{\rho_1}$, completing the proof of Theorem 4.1. In order to derive the aforementioned lower bound to $\psi(x_1,x_2)$ we first need Theorem 4.3.

Theorem 4.3. Let $r_2\leq b$, b some positive constant, then there is a constant $C_b>0$, such that

$$\psi(x_1,x_2)\geq C_b[\rho_1(x_1)]^{1/2},\quad\forall x_1\in\mathbb{R}^3. \tag{4.18}$$

Remark 4.4. The upper bound to $\psi(x_1,x_2)$ (Lemma 3.2), implies that for $r_2\leq b$ there are two constants $0<C_-<C_+<\infty$, such that

$$C_-[\rho_1(x_1)]^{1/2}\leq\psi(x_1,x_2)\leq C_+[\rho_1(x_1)]^{1/2}, \tag{4.19}$$

or more explicitly: there are two positive constants K_+ and K_- with $0<K_-<K_+<\infty$, such that

$$K_-(1+r_1)^{(Z-1)/\sqrt{2\epsilon_1}-1}e^{-\sqrt{2\epsilon_1}r_1}\leq\psi(x_1,x_2)\leq K_+(1+r_1)^{(Z-1)/\sqrt{2\epsilon_1}-1}e^{-\sqrt{2\epsilon_1}r_1}. \tag{4.20}$$

Proof. The main idea behind the proof resembles closely some arguments given in IV. We combine Theorem 4.2 with Corollary 4.1, and first prove (4.18) with $r_2=0$. Let $B^{(6)}(y,2R)$ denote a ball in $\mathbb{R}^6$ with radius $2R$ centered at $y=(x_1,0)$. By Theorem 2.4 we have

$$\inf_{(x_1',x_2')\in B^{(6)}(y,2R)}\psi(x_1',x_2')\geq K_{2R}\sup_{(x_1',x_2')\in B^{(6)}(y,2R)}\psi(x_1',x_2'). \tag{4.21}$$

Equation (4.21) implies for $(x_1,x_2)\in B^{(6)}(y,2R)$ with some elementary inequalities

$$\begin{aligned}\psi^2(x_1,x_2)&\geq K_{2R}^2\sup_{(x_1',x_2')\in B^{(6)}(y,2R)}\psi^2(x_1',x_2')\geq K_{2R}^2\sup_{|x_1-x_1'|\leq R;\ r_2'\leq R}\psi^2(x_1',x_2')\\&\geq K_{2R}^2\left(\frac{4\pi R^3}{3}\right)^{-1}\sup_{|x_1'-x_1|\leq R}\int_{r_2'\leq R}\psi^2(x_1',x_2')dx_2'\\&\geq K_{2R}^2\left(\frac{4\pi R^3}{3}\right)^{-1}\left(\int_{r_2\leq R}\psi(x_1,x_2)\phi(x_2)dx_2\right)^2\left(\int_{r_2\leq R}\phi^2(x_2)dx_2\right)^{-1}.\end{aligned} \tag{4.22}$$

Absorbing the R dependence in the positive constant A_R, we obtain

$$\psi(x_1, 0) \geq A_R \int_{r_2 \leq R} \psi(x_1, x_2)\phi(x_2)dx_2 . \qquad (4.23)$$

But

$$\int_{r_2 \leq R} \psi(x_1, x_2)\phi(x_2)dx_2 = u(x_1) - \int_{r_2 > R} \psi(x_1, x_2)\phi(x_2)dx_2 . \qquad (4.24)$$

Using the Cauchy-Schwarz inequality and an L^∞ estimate, we obtain

$$\int_{r_2 \geq R} \psi(x_1, x_2)\phi(x_2)dx_2 \leq \left(\rho_1(x_1)\int_{r_2 \geq R} \phi^2(x_2)dx_2\right)^{1/2} \leq C[\rho_1(x_1)]^{1/2}e^{-ZR/2} \qquad (4.25)$$

for some constant $C < \infty$.

Now Corollary 4.1 implies that for some constant $K > 0$,

$$u(x_1) \geq K[\rho_1(x_1)]^{1/2} . \qquad (4.26)$$

Therefore, by choosing R in (4.25) large enough, we obtain

$$\int_{r_2 \leq R} \psi(x_1, x_1)\phi(x_2)dx_2 \geq C_R[\rho_1(x_1)]^{1/2} \qquad (4.27)$$

and furthermore by (4.23) for some constant B

$$\psi(x_1, 0) \geq B[\rho_1(x_1)]^{1/2} . \qquad (4.28)$$

Another obvious application of (4.21) leads to (4.18).

We finally derive a nonisotropic lower bound for $\psi(x_1, x_2)$, the main result of this section.

Theorem 4.4. Let

$$f(u) = \sum_{k=0,\infty} \frac{u^k}{k!(k+1)!}, \quad u \in \mathbb{R} \qquad (4.29)$$

$$F(r_1, r_2, r_{12}) = (1 + r_1)^\alpha e^{-\sqrt{2\epsilon_1}\, r_1 - Zr_2} f(r_{12})/f(r_1 + r_2) , \qquad (4.30)$$

$$\alpha = (Z-1)/\sqrt{2\epsilon_1} - 1 , \qquad (4.31)$$

$$v(r_1, r_2, r_{12}) = \begin{Bmatrix} F(r_1, r_2, r_{12}) & r_1 \geq r_2 \\ F(r_2, r_1, r_{12}) & r_1 \leq r_2 \end{Bmatrix}, \qquad (4.32)$$

then

$$\psi(x_1, x_2) \geq Cv(r_1, r_2, r_{12}), \quad \forall (x_1, x_2) \in \mathbb{R}^6 \qquad (4.33)$$

for suitably chosen $C > 0$.

Remark 4.5. The function $f(u)$, defined in (4.29), is a solution of the differential equation

$$f''(u) + \frac{2}{u}f'(u) = \frac{1}{u}f(u) . \qquad (4.34)$$

f is related to the Bessel function J_1 (Ref. 15):

$$f(u) = \frac{1}{i\sqrt{u}} J_1(2i\sqrt{u}) . \qquad (4.35)$$

We note without proof the following properties of f, which will be used below:

$$f(u) = \sqrt{4\pi^{-1}}u^{-3/4}e^{2\sqrt{u}}[1 + O(u^{-1/2})] , \qquad (4.36)$$

$$\frac{f'(u)}{f(u)} = u^{-1/2}[1 + O(u^{-1/2})] , \qquad (4.37)$$

$$0 \leq u_1 \frac{f'(u_1)}{f(u_1)} \leq u_2 \frac{f'(u_2)}{f(u_2)} \text{ for } 0 \leq u_1 \leq u_2 . \qquad (4.38)$$

Proof of Theorem 4.4. We have only to prove (4.33) in the region Ω,

$$\Omega = \{(x_1, x_2) \in \mathbb{R}^6 : r_1 \geq b,\ r_2 \geq b\}, \quad b > 0 \qquad (4.39)$$

since (4.33) holds in $\mathbb{R}^6 \backslash \Omega$ by means of Theorem 4.3 and (4.20). Let

$$\tilde{F}(r_1, r_2, r_{12}) = r_1^\alpha e^{-\sqrt{2\epsilon_1}r_1 - Zr_2} f(r_{12})/f(r_1 + r_2) , \qquad (4.40)$$

$$g(r_1, r_2) = (1 + ar_1^{-\gamma})(1 + ar_2^{-\gamma}), \quad \gamma > 0 , \qquad (4.41)$$

and

$$\tilde{v}(r_1, r_2, r_{12}) = \begin{cases} \tilde{F}(r_1, r_2, r_{12})g(r_1, r_2), & r_1 \geq r_2 \\ \tilde{F}(r_2, r_1, r_{12})g(r_1, r_2), & r_2 \geq r_1 . \end{cases} \qquad (4.42)$$

We use Theorem 2.1 to prove that

$$\psi(x_1, x_2) \geq C\tilde{v}(r_1, r_2, r_{12}) \text{ in } \Omega , \qquad (4.43)$$

from which (4.33) follows immediately. For the application of Theorem 2.1 we first note that

$$\psi(x_1, x_2) \geq C\tilde{v}(r_1, r_2, r_{12}) \text{ for } (x_1, x_2) \in \partial\Omega . \qquad (4.44)$$

This follows directly from the definition of $\tilde{v}$ and the properties of f—as discussed in Remark 4.5—together with (4.20). It then only remains to show that

$$(H - E)\tilde{v} \leq 0 \text{ in } \Omega , \qquad (4.45)$$

which is verified in Appendix B.

Remark 4.6. As we are concerned here with a two-electron system the upper bound (3.19) for $\sqrt{\rho_2}$ is actually an upper bound for $\psi(x_1, x_2)$. We may therefore use the Theorems 3.3 and 4.4 to bracket the ground state wave function for two-electron systems. If we consider again only $r_1 \geq r_2$, (3.19) and (4.33) (together with $\sqrt{2\epsilon_2} = Z$, $n = 2$) yield

$$C_-(1+r_1)^\alpha e^{-\sqrt{2\epsilon_1}r_1-Zr_2}f(r_{12})/f(r_1+r_2)$$
$$\leq \psi(x_1,x_2)$$
$$\leq C_+(1+r_1)^\alpha(1+r_2)^\beta e^{-\sqrt{2\epsilon_1}r_1-Zr_2}, \quad (4.46)$$

with α as in (4.31), $\beta > 1/2Z$, and appropriately chosen constants C_- and C_+. The upper and lower bounds agree in the exponential terms and, up to $(1+r_2)^\beta$, also in the pre-exponential factors. The only noticeable deviation between upper and lower bounds is the term $f(r_{12})/f(r_1+r_2)$, which may, using the properties of f described in Remark 4.5, be approximated as

$$f(r_{12})/f(r_1+r_2) \approx e^{-(r_1+r_2-r_{12})/(r_1+r_2)^{1/2}},$$
$$\text{if } r_1+r_2-r_{12} \ll r_1+r_2 \quad (4.47)$$

$$f(r_{12})/f(r_1+r_2) \approx e^{-2\sqrt{r_1+r_2}}, \quad \text{if } r_{12} \ll r_1+r_2 \quad (4.48)$$

provided r_1+r_2 is large. If $r_{12} \approx r_1+r_2$ (i.e., if $r_1/r_2 \gg 1$ or if the electrons are on opposite sides of the nucleus: $x_1/r_1 \approx -x_2/r_2$), then $f(r_{12})/f(r_1+r_2) \approx 1$, see (4.47). $f(r_{12})/f(r_1+r_2)$ decays as $e^{-\sqrt{r_1+r_2}}$ if $r_{12} \approx 0$ and $r_1 \approx r_2 \to \infty$, see (4.48), and the lower bound to $\psi(x_1,x_2)$ shows a correspondingly faster decay than the upper bound in these regions of configuration space.

Remark 4.7. As is seen from the derivation of the above Theorems (4.1–4.3), the multiplicative constants are not evaluated explicitly. At the moment the possibility of overcoming this deficiency seems small. The only explicit lower bound for $\sqrt{\rho_1}$ is given in the recent book by Thirring[20] where a lower bound to the one-electron density of the ground state of two-electron atoms at the nucleus is derived.

V. DISCUSSION

Let us finally discuss the quality of our results. We consider the asymptotics of the upper bounds to the one-electron density to be optimal. This opinion is very strongly supported by the lower bound (Theorem 4.1) to the one-electron density of the ground state of two-electron atoms. However, our techniques for lower bounds are still restricted to positive ground states and it seems in the moment difficult to overcome this restriction.

Recently it has been demonstrated by Carlton[21] that a knowledge of the asymptotic behavior of ρ_1 is also very useful from a numerical point of view. He used (4.2) to test the reliability of accurately computed one-electron densities far from the nucleus; he also observed that the behavior described by (4.2) extends to regions near the nucleus. But inequality (4.2) also prompts us to advance the following conjecture which is based on a rather plausible physical picture. (We use the notation of Sec. IV).

Conjecture. For every fixed x_2

$$\lim_{|x_1|\to\infty} \psi(x_1,x_2)[\rho_1(x_1)]^{-1/2} \to \phi(x_2) \quad (5.1)$$

and

$$\lim_{|x_1|\to\infty} u(x_1)[\rho_1(x_1)]^{-1/2} = 1\,. \quad (5.2)$$

The following argument provides support for (5.1). If we let r_1 approach infinity in $\psi(x_1,x_2)$, the remainder should behave as $\phi(x_2)$, the ground state of the ionized system, the $\sqrt{\rho_1}$ in the denominator simply assures normalization. A proof of this conjecture seems to be rather difficult since problems arise in keeping track of quotients. Relations analogous to (5.1) and (5.2) should hold in many-electron systems, but due to the lack of positivity of ψ, the situation would be even more complicated.

As a last remark concerning the bounds to the one-electron densities, we consider the case of atomic anions with charge -1. The pre-exponential in (4.2) is then independent of ϵ_1 and Z, a situation which appears to be typical for short-range potentials.[7,17] Indeed, in such a system an electron far from the nucleus "sees" a neutral atom and "feels" an effective short-range potential.

Let us now consider the upper bounds for the many-electron densities. The condition (1.6) $\epsilon_1 \leq \epsilon_2$ is not necessary in order to obtain the upper bounds (3.2). But, if $\epsilon_1 > \epsilon_2$, for example, it is easily seen that our bounds are rather weak. Although, (1.6) is invariably observed experimentally, it is unfortunate that its proof is still missing. Morgan, Lieb, and Simon[22] demonstrated the delicate nature of this problem by constructing several model Hamiltonians closely related to atomic Hamiltonians where $\epsilon_1 > \epsilon_2$.

At the first glance (3.2) seems to be quite satisfactory. However, Theorem 3.2 shows that the screening effects in the pre-exponential factors are more complicated than was earlier suspected (II). The situation is also obscured by the lack of a simple picture which explains many particle screening effects.

Note added in proof. Since the submission of our paper the following relevant unpublished work and papers have come to our attention: Upper bounds: S. Agmon, Proc. A. Pleijel Conference, Uppsala 1979; unpublished. Lower bounds: R. Carmona and B. Simon, unpublished. Results in relation with (5.1) and (5.2): E. H. Lieb and B. Simon, Adv. Appl. Math. 1, 324 (1980), J. M. Combes, M. Hoffmann-Ostenhof, and T. Hoffmann-

Ostenhof, J. Math. Phys., in press, J. Katriel and E. R. Davidson, Proc. Natl. Acad. Sci. USA 77, 4403 (1980).

ACKNOWLEDGMENTS

Two of us (Maria Hoffmann-Ostenhof and Thomas Hoffmann-Ostenhof) express their gratitude to P. Schuster and W. Thirring for continuous interest and support. We thank B. Simon for helpful discussions, and P. Taylor for comments on the the manuscript. Part of this work was supported by "Fonds zur Fördenrung der Wissenschaftlichen Forschung in Österreich", Project No. 3655, 2740 and by the "Fonds der Chemischen Industrie". J. M. is the recipient of a Chaim Weizmann Postdoctoral Fellowship.

APPENDIX A: PROOF OF THEOREM 3.2

By Lemma 3.1 we have

$$L[\rho_2(x_1,x_2)]^{1/2}\leqslant 0 \text{ for } (x_1,x_2)\in\Omega\,, \tag{A1}$$

where

$$L=\sum_{i=1,2}\left(-\frac{\Delta_i}{2}-\frac{Z-n+2}{r_i}-\frac{d}{r_i^2}+\epsilon_i\right)+\frac{1}{r_{12}}\,, \tag{A2}$$

with $d>0$ a constant and

$$\Omega=\{(x_1,x_2)\in\mathbb{R}^6: r_1,r_2\geqslant a\}\,,$$

with a sufficiently large. Let

$$\begin{aligned}F(r_1,r_2)&=C\,r_1^{\beta-1}r_2^{\alpha-1}e^{-\sqrt{2\epsilon_2}r_1-\sqrt{2\epsilon_1}r_2}\,,\\ v(x_1,x_2)&=F(r_1,r_2)+F(r_2,r_1),\end{aligned} \tag{A3}$$

with α,β defined according to (3.19). Suppose we have shown that

$$Lv\geqslant 0 \text{ in } \Omega\,. \tag{A4}$$

Then since $\sqrt{\rho_2}\leqslant v$ on $\partial\Omega$ (this follows analogously as in Theorem 3.1 via Lemma 3.2), Theorem 2.1 implies that (3.19) holds in Ω. In $\mathbb{R}^6\backslash\Omega$ (3.19) results again by Lemma 3.2 and the boundedness of ρ_2.

We shall now sketch the proof of (A4): By a straightforward calculation we have

$$\frac{Lv}{v}=\left(A(1,2)+\frac{1}{r_{12}}\right)B(1,2)+\left(A(2,1)+\frac{1}{r_{12}}\right)B(2,1), \tag{A5}$$

where

$$\begin{aligned}A(1,2)&=-\frac{\beta(\beta-1)}{2r_1^2}+\frac{\beta\sqrt{2\epsilon_2}-Z+n-2}{r_1}-\frac{\alpha(\alpha-1)}{2r_2^2}-\frac{1}{r_2}\,,\\ B(1,2)&=F(r_1,r_2)/v\,,\end{aligned} \tag{A6}$$

$[A(1,2), A(2,1)$ is shorthand notation for $A(r_1,r_2)$, $A(r_2,r_1)$, analogously for $B]$. Clearly,

$$B(1,2)\geqslant 0,\quad B(2,1)\geqslant 0,\quad B(1,2)+B(2,1)=1\,. \tag{A7}$$

Without loss of generality we consider the case $r_1\leqslant r_2$. Then with $r_{12}^{-1}\geqslant (r_1+r_2)^{-1}$, and the definition of β it is easily seen that

$$r_1\left(\frac{1}{r_{12}}+A(1,2)\right)\geqslant\beta\sqrt{2\epsilon_2}-Z+n-2-\tfrac{1}{2}-\delta_1>0\,, \tag{A8}$$

$$r_1\left(\frac{1}{r_{12}}+A(2,1)\right)\geqslant[\beta\sqrt{2\epsilon_2}-Z+n-2-\delta_2)\frac{r_1}{r_2}-\frac{r_2}{r_1+r_2}-\delta_3\,, \tag{A9}$$

with δ_1, δ_2, δ_3 arbitrarily small.

Let $1\leqslant r_2/r_1\leqslant 1+m$ $(m>0)$, then (A9) implies

$$r_1\left(\frac{1}{r_{12}}+A(2,1)\right)\geqslant(\beta\sqrt{2\epsilon_2}-Z+n-2-\delta_2)\frac{1}{m+1}-\frac{m+1}{m+2}-\delta_3\,. \tag{A10}$$

The rhs of this inequality is continuous and monotonically nonincreasing for $m\geqslant 0$, and is positive for $m=0$. Therefore an $m_0>0$ exists such that

$$r_1\left(\frac{1}{r_{12}}+A(2,1)\right)>0\,. \tag{A11}$$

Combining (A5), (A7), (A10), and (A11)

$$Lv\geqslant 0 \text{ for } 1\leqslant r_2/r_1\leqslant 1+m_0 \tag{A12}$$

results.

(ii) For $1+m_0\leqslant r_2/r_1$ we conclude from (A9) that

$$r_1\left(\frac{1}{r_{12}}+A(2,1)\right)\geqslant-(1+\delta_3)\,. \tag{A13}$$

Hence by (A8) and (A13) it remains to show that

$$B(1,2)d_1-B(2,1)d_2\geqslant 0\quad(d_1,d_2>0)\,. \tag{A14}$$

But this follows easily by writing

$$r_2=(1+m_0)r_1+y\quad(y\geqslant 0)\,. \tag{A15}$$

Finally by (i) and (ii), (A4) results.

APPENDIX B: PROOF OF INEQUALITY (4.45)

It is obviously sufficient to consider the case $r_1 \geq r_2$. At $r_1 = r_2$ $\tilde{v}$ has discontinuous derivatives, but $(-\Delta_1 - \Delta_2)\tilde{v} = -\infty$ at these points. Now we consider

$$\frac{(H-E)\tilde{F}g}{\tilde{F}g} = \frac{(H-E)\tilde{F}}{\tilde{F}} + J\,, \tag{B1}$$

and shall show that

$$\frac{(H-E)\tilde{F}}{\tilde{F}} \leq O\left(\frac{1}{r_1^{1+\delta}}\right) + O\left(\frac{1}{r_2^{1+\delta}}\right) \quad (\delta > 0)\,, \tag{B2}$$

and

$$J \leq -\left(\frac{1}{r_1^{1+\gamma}} + \frac{1}{r_2^{1+\gamma}}\right) K, \quad \text{with some } K > 0\,, \tag{B3}$$

for r_1, r_2 sufficiently large. For $0 < \gamma < \delta$ this implies (4.45). Let us first verify (B2): A somewhat tedious analysis yields

$$\begin{aligned}\tilde{F}^{-1}(H-E)\tilde{F} = {} & -2\left|\frac{f'(r_1+r_2)}{f(r_1+r_2)}\right|^2 + \frac{f''(r_1+r_2)}{f(r_1+r_2)} - Z\sqrt{2\epsilon_1}\,\frac{f'(r_1+r_2)}{f(r_1+r_2)} \\ & + \frac{f'(r_{12})}{f(r_{12})}\left[(A+B)\left(\sqrt{2\epsilon_1} + \frac{f'(r_1+r_2)}{f(r_1+r_2)}\right) + (Z-\sqrt{2\epsilon_1})B - A\,\frac{\alpha}{r_1}\right] \\ & - \frac{\alpha(\alpha+1)}{2r_1^2} + \frac{f'(r_1+r_2)}{f(r_1+r_2)}\left(\frac{1+\alpha}{r_1} + \frac{1}{r_2}\right) - \frac{1}{r_1}\,,\end{aligned} \tag{B4}$$

where

$$A = (r_{12}^2 + r_1^2 - r_2^2)/(2r_{12}r_1)\,, \tag{B5}$$

$$B = (r_{12}^2 + r_2^2 - r_1^2)/(2r_{12}r_2)\,. \tag{B6}$$

In the derivation of (B4) we have used $E = -Z^2/2 - \epsilon_1$, the differential equation (4.34), and the definition (4.31) of α. Inserting the (easily proven) bounds

$$A + B \leq \frac{2r_{12}}{r_1 + r_2}\,, \tag{B7}$$

$$B \leq \frac{r_{12}}{r_1 + r_2} \text{ for } r_1 \geq r_2\,, \tag{B8}$$

and using (4.38) with $u_1 = r_{12} \leq (r_1 + r_2) = u_2$, we obtain

$$\tilde{F}^{-1}(H-E)\tilde{F} \leq \frac{f''(r_1+r_2)}{f(r_1+r_2)} + \frac{f'(r_1+r_2)}{f(r_1+r_2)}\left(\frac{1}{r_2} + \frac{Z-1}{\sqrt{2\epsilon_1}\,r_1}\right) - \frac{1}{r_1}\,. \tag{B9}$$

Finally the differential equation (4.34) for f together with the asymptotic property (4.37) of f'/f yields (B2).

We now show (B3): By a straightforward calculation we have

$$\mathrm{J} = \frac{a\gamma}{(1+ar_1^{-\gamma})r_1^{\gamma+1}}\left(\frac{1-\gamma}{2r_1} + \frac{\alpha}{r_1} - \sqrt{2\epsilon_1} - \frac{f'(r_1+r_2)}{f(r_1+r_2)} + A\right) + \frac{a\gamma}{(1+ar_2^{-\gamma})r_2^{\gamma+1}}\left(\frac{1-\gamma}{2r_2} - Z - \frac{f'(r_1+r_2)}{f(r_1+r_2)} + B\right)\,. \tag{B10}$$

Using (4.38) as before we obtain

$$\mathrm{J} \leq -K(r_1^{-\gamma-1} + r_2^{-\gamma-1}) + \frac{f'(r_{12})}{f(r_{12})}\,\frac{(r_1-r_2)[(r_1+r_2)^2 - r_{12}^2]}{2r_{12}(r_1+r_2)}\left(\frac{1}{r_1^{\gamma+2}(1+ar_1^{-\gamma})} - \frac{1}{r_2^{\gamma+2}(1+ar_2^{-\gamma})}\right)\,. \tag{B11}$$

For $r_1 \geq r_2$ (B11) now implies (B3) using again (4.38).

[1]M. Hoffmann-Ostenhof and T. Hoffmann-Ostenhof, Phys. Rev. A 16, 1782 (1977).

[2]T. Hoffmann-Ostenhof, M. Hoffmann-Ostenhof, and R. Ahlrichs, Phys. Rev. A 18, 328 (1978).

[3]T. Hoffmann-Ostenhof, J. Phys. A 12, 1181 (1979).

[4]T. Hoffmann-Ostenhof, Phys. Lett. A 77, 142 (1980).

[5]P. Deift, W. Hunziker, B. Simon, and E. Vock, Commun. Math. Phys. 64, 1 (1978).

[6]T. Hoffmann-Ostenhof, J. Phys. A 13, 417 (1980).

[7]J. Morgan, J. Math. Phys. 19, 1658 (1978).

[8]N. S. Trudinger, Ann. Scuola Norm. Sup. Pisa (3), 27, 265 (1973).

[9]D. Gilbarg and N. S. Trudinger, *Elliptic Partial Differential Equations of Second Order* (Academic, New

York, 1970).

[10]M. Hoffmann-Ostenhof, T. Hoffmann-Ostenhof, and B. Simon, J. Phys. A 13, 1131 (1980).

[11]M. Hoffmann-Ostenhof, T. Hoffmann-Ostenhof, and B. Simon, Proc. Am. Math. Soc. 80, 301 (1980).

[12]B. Simon, *Functional Integration and Quantum Physics* (Academic, New York, 1979).

[13]M. Reed and B. Simon, *Methods of Modern Mathematical Physics IV: Analysis of Operators* (Academic, New York, 1978).

[14]J. Morgan III and B. Simon, Int. J. Quantum Chem. XVII, 1143 (1980).

[15]M. Abramowitz and I. A. Stegun, *Handbook of Mathematical Functions*, U. S. Natl. Bur. Stand. (Appl. Math. Ser. No. 55), edited by M. Abramowitz and I. A. Stegun (U. S. G. P. O., Washington, D.C., 1964).

[16]B. Simon, Trans. Am. Math. Soc. 208, 317 (1974).

[17]S. P. Merkuriev, Sov. J. Nucl. Phys. 19, 222 (1974).

[18]C. Bardos and M. Merigot, Proc. R. Soc. Edinburgh 76A, 323 (1977).

[19]R. Carmona, Commun. Math. Phys. 62, 97 (1978).

[20]W. Thirring, *Lehrbuch der Mathem. Physik III* (Springer, Vienna, 1979).

[21]Carlton, J. Chem. Phys. 70, 584 (1979).

[22]J. Morgan III, Berkeley thesis, 1979 (unpublished).