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Lower and upper bounds to the decay of the ground state one-electron density of helium-like systems

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Abstract. The asymptotic behaviour of the ground state one-electron density $\rho(x)$ of two-electron atoms is investigated. Lower and upper bounds to $\rho(x)$ showing 'almost' the same decay are derived.

1. Introduction

We consider a two-electron atomic system described by the Hamiltonian

$$H=-\frac{\Delta_1}{2}-\frac{\Delta_2}{2}-\frac{Z}{r_1}-\frac{Z}{r_2}+|x_1-x_2|^{-1}, \qquad x_i\in R^3, |x_i|=r_i, i=1,2, \tag{1.1}$$

where Z denotes the nuclear charge. The ground state electron density $\rho(x)$ is defined by

$$\rho(x_1)=\int|\psi(x_1,x_2)|^2\,\mathrm{d}x_2, \tag{1.2}$$

where ψ is normalised to 1 and satisfies the Schrödinger equation $H\psi=E\psi$, where E is the ground state energy. Note that $\rho(x)=\rho(|x|)$.

Asymptotic properties of subcontinuum wavefunctions of quantum mechanical systems have been recently investigated rather intensively. (See Hoffmann-Ostenhof *et al* (1978) and Deift *et al* (1978) for recent results and references to other work.) For many-particle systems, however, only upper bounds are available, except for the results of Mercuriev (1974) on three-particle systems with short-range potentials. For the one-particle case Simon (1975) and Bardos and Merigot (1977) obtained lower bounds.

For atomic one-electron densities Hoffmann-Ostenhof and Hoffmann-Ostenhof (1977) derived an upper bound

$$\sqrt{\rho(x)}\leqslant kr^{Z/\sqrt{2\epsilon}-1}\,\mathrm{e}^{-\sqrt{2\epsilon}r}, \qquad k<\infty \tag{1.3}$$

for sufficiently large r, where ϵ denotes the ionisation energy. (For a definition of ϵ see for instance Hoffmann-Ostenhof and Hoffmann-Ostenhof (1977).) It was then conjectured that the nuclear charge Z in (1.3) could be replaced by $Z-(n-1)$, where n denotes the number of electrons, such that

$$\sqrt{\rho(x)}\leqslant k'r^{(Z-n+1)/\sqrt{2\epsilon}-1}\,\mathrm{e}^{-\sqrt{2\epsilon}r}, \qquad k'<\infty \tag{1.4}$$

to account for electron shielding.

We shall prove (1.4) in § 3 for two-electron atoms. In § 2 we shall give a lower bound to $\rho(x)$ which decays only slightly faster than the right-hand side of (1.4).

Our subsequent considerations will be based on a comparison theorem for differential inequalities which had been used for the investigation of the decay of many-particle subcontinuum wavefunctions by Deift *et al* (1978) and Hoffmann-Ostenhof *et al* (1978). We cite its shortest version due to Deift *et al* (1978).

Theorem 1.1. Let f, g be continuous functions and let $V \geqslant W \geqslant 0$ on $\overline{R^n \backslash S}$ for some closed set S. Suppose that on $R^n \backslash S$, in the distributional sense $\Delta|g| \geqslant V|g|$ and $\Delta|f| \leqslant W|f|$ and that $|g| \leqslant |f|$ on ∂S and $f, g \to 0$ as $|x| \to \infty$. Then $|g| \leqslant |f|$ on $R^n \backslash S$.

2. Lower bounds

Let $\phi_R(x)$ be the normalised and radially symmetric ground state of a hydrogenic system confined in a ball with radius R; that means, we impose the boundary condition $\phi_R(R) = 0$ on the corresponding Schrödinger equation which reads

$$\left(-\frac{\Delta}{2} - \frac{Z}{r}\right)\phi_R(x) = E_R \phi_R(x), \tag{2.1}$$

where E_R is the ground state energy depending on R. The variational principle implies

$$E_R \geqslant E_\infty = -Z^2/2. \tag{2.2}$$

Let

$$u_R(x_1) = \int \phi_R(x_2)\psi(x_1, x_2)\, \mathrm{d}x_2. \tag{2.3}$$

Since $\phi_R(x_2)$ and $\psi(x_1, x_2)$ are ground states without symmetry restrictions, they are both strictly positive for finite r_1, r_2 (see e.g. Reed and Simon 1978), and consequently $u_R > 0$ for finite r_1. Note also that u_R is radially symmetric. We are now going to derive a non-negative lower bound to $u_R(r)$ which is in turn a lower bound to $\sqrt{\rho(r)}$, since

$$u_R(r) \leqslant \sqrt{\rho(r)} \tag{2.4}$$

due to the Cauchy–Schwarz inequality.

Lemma 2.1.

$$\left(-\frac{\Delta}{2} - \frac{Z-1}{r} + E_R - E + R(\alpha - 1)^{-1} r^{-2}\right) u_R(x) \geqslant 0 \tag{2.5}$$

for $r \geqslant \alpha R$ and $\alpha > 1$.

Proof. Starting from

$$\int \phi_R(x_2)(H - E)\psi(x_1, x_2)\, \mathrm{d}x_2 = 0 \tag{2.6}$$

we obtain applying Green's formula

$$\left(-\frac{\Delta_1}{2}-\frac{Z}{r_1}-E+E_R\right)u_R(x_1)+\int \phi_R(x_2)\psi(x_1, x_2)|x_1-x_2|^{-1}\,dx_2$$

$$+\int_{\sigma(R)}\left(\phi_R\frac{\partial\psi}{\partial n}-\psi\frac{\partial\phi_R}{\partial n}\right)d\sigma=0. \tag{2.7}$$

Since $\phi_R\psi \geqslant 0$, we get

$$\int \phi_R\psi|x-x_2|^{-1}\,dx_2 \leqslant u_R(r_1-R)^{-1} \leqslant u_R r_1^{-1}[1+R(\alpha-1)^{-1}r_1^{-1}] \tag{2.8}$$

for $r_1 \geqslant \alpha R$, $\alpha > 1$. The surface term in (2.7) is obviously negative, since

$$\int_{\sigma(R)} \phi_R\frac{\partial\psi}{\partial n}\,d\sigma=0 \tag{2.9}$$

and

$$-\int_{\sigma(R)}\psi\frac{\partial\phi_R}{\partial n}\,d\sigma=\left.\frac{d\phi_R}{dr_2}\right|_{r_2=R-0}\int_{\sigma(R)}\psi\,d\sigma\leqslant 0. \tag{2.10}$$

Combining (2.8), (2.9) and (2.10) with (2.7) we obtain inequality (2.5).

Now we use lemma 2.1 and theorem 1.1 to derive the following lower bound to $\sqrt{\rho}$.

Theorem 2.1. There exists for every $\delta>0$ a $K_\delta>0$ such that for sufficiently large r_0

$$\sqrt{\rho(r)} \geqslant K_\delta r^{(Z-1)/\sqrt{2(\epsilon+\delta)}-1}\,e^{-\sqrt{2(\epsilon+\delta)}r} \tag{2.11}$$

for $r \geqslant r_0$; ϵ denotes the ionisation energy $-Z^2/2-E$.

Proof. Since E_R decreases monotonically to $E_\infty=-Z^2/2$, we can find for every $\delta>0$ an R_δ such that for all $R \geqslant R_\delta$, $E_R-E<\epsilon+\delta$, which implies via lemma 2.1

$$\left(-\frac{\Delta}{2}-\frac{Z-1}{r}+\epsilon+\delta+R(\alpha-1)^{-1}r^{-2}\right)u_R(x)\geqslant 0 \qquad \text{for } r\geqslant\alpha R, \tag{2.12}$$

where $R \geqslant R_\delta$, $\alpha>1$.

Suppose we find a function $v(r)$ satisfying

$$\left(-\frac{\Delta}{2}-\frac{Z-1}{r}+\epsilon+\delta+R(\alpha-1)^{-1}r^{-2}\right)v(x)\leqslant 0 \qquad \text{for } r\geqslant r_0 \tag{2.13}$$

with r_0 sufficiently large so that

$$r_0 \geqslant \alpha R \tag{2.14}$$

and

$$-\frac{Z-1}{r}+\epsilon+\delta+R(\alpha-1)^{-1}r^{-2}\geqslant 0 \qquad \text{for } r\geqslant r_0. \tag{2.15}$$

If in addition

$$v(r_0)<u_R(r_0) \tag{2.16}$$

holds, then we can conclude by theorem 1.1 that

$$v(r) \leqslant u_R(r) \qquad \text{for } r \geqslant r_0. \tag{2.17}$$

With the *ansatz*

$$v = C_\delta r^{(Z-1)/\sqrt{2(\epsilon+\delta)}-1} \, \mathrm{e}^{-\sqrt{2(\epsilon+\delta)}r}(1-b_\delta/r), \tag{2.18}$$

where b_δ and C_δ are constants, a straightforward computation of the left-hand side of (2.13) shows that the expression obtained is non-positive for suitably chosen $b_\delta > 0$ and for r_0 sufficiently large. (Obviously $r_0 > b_\delta$ is necessary for $v(x)$ to be positive.) Since u_R is positive for finite r, we can choose a $C_\delta > 0$ so that the boundary condition (2.16) is fulfilled. Hence we have proven inequality (2.17), and therefrom (2.11) follows immediately.

3. Upper bounds

Let $h(x_1)$ denote the operator depending parametrically on x_1,

$$h(x_1) = -\frac{\Delta_2}{2} - \frac{Z}{r_2} + |x_1 - x_2|^{-1}, \tag{3.1}$$

which is self-adjoint on the domain $D(-\Delta_2)$. Let $F(x_1)$ be the bottom of the spectrum of $h(x_1)$. Then the variational principle implies

$$\int \psi(x_1, x_2) h(x_1) \psi(x_1, x_2) \, \mathrm{d}x_2 \geqslant F(x_1)\rho(x_1). \tag{3.2}$$

We shall prove the following differential inequality which holds in the distributional sense.

Lemma 3.1.

$$\left(-\frac{\Delta}{2} - \frac{Z}{r} + F(x) - E\right)\sqrt{\rho(x)} \leqslant 0 \tag{3.3}$$

Proof. Since

$$0 = \int \psi(H-E)\psi \, \mathrm{d}x_2 = \int \psi\left(-\frac{\Delta_1}{2} - \frac{Z}{r_1} + h(x_1) - E\right)\psi \, \mathrm{d}x_2, \tag{3.4}$$

(3.2) together with

$$-\int \psi \Delta_1 \psi \, \mathrm{d}x_2 \geqslant -\sqrt{\rho(x_1)}\Delta_1\sqrt{\rho(x_1)} \tag{3.5}$$

(see Hoffmann-Ostenhof and Hoffmann-Ostenhof 1977) immediately leads to (3.3).

In order to apply theorem 1.1 we need an explicit expression for $F(x)$, namely a lower bound. Let

$$\phi(x_2) = Z^{3/2} \pi^{-1/2} \, \mathrm{e}^{-Zr_2}; \tag{3.6}$$

then we obtain, applying Cauchy–Schwarz's inequality,

$$F(x_1)\geqslant \inf_{\substack{\chi(x_2)\\ \|\chi\|=1}}\left[\int \chi(x_2)\left(-\frac{\Delta_2}{2}-\frac{Z}{r_2}\right)\chi(x_2)\,\mathrm{d}x_2+\left|\int \phi\chi\,\mathrm{d}x_2\right|^2 m(x_1)\right], \tag{3.7}$$

$$m(x_1)=(\textstyle\int\phi^2|x_1-x_2|\,\mathrm{d}x_2)^{-1}.$$

For r_0 sufficiently large so that

$$m(x_1)\leqslant 3Z^2/8 \qquad \text{for } r\geqslant r_0, \tag{3.8}$$

(3.7) becomes

$$F(x_1)\geqslant -Z^2/2+m(x_1), \tag{2.9}$$

observing that $\phi(x_2)$ is the ground state of

$$-\frac{\Delta_2}{2}-\frac{Z}{r_2}+m(x_1)|\phi(x_2)\rangle\langle\phi(x_2)| \tag{3.10}$$

provided (3.8) holds. A computation shows that

$$m(x)=r^{-1}[1+Z^{-2}r^{-1}-(Z^{-1}r^{-1}/2+Z^{-2}r^{-2})\,\mathrm{e}^{-Zr}]^{-1}\geqslant r^{-1}(1-Z^{-2}r^{-2}). \tag{3.11}$$

Combination of (3.9) and (3.11) with (3.3) leads to

$$-\frac{\Delta}{2}\sqrt{\rho}+\left(\epsilon-\frac{Z-1}{r}-Z^{-2}r^{-3}\right)\sqrt{\rho}\leqslant 0, \qquad r\geqslant r_0 \tag{3.12}$$

with r_0 chosen according to (3.8). If we find a function $v(r)$ satisfying

$$-\frac{\Delta}{2}v+\left(\epsilon-\frac{Z-1}{r}-Z^{-2}r^{-3}\right)v\geqslant 0 \qquad \text{for } r\geqslant r_0 \tag{3.13}$$

with r_0 sufficiently large so that (3.8) and

$$\epsilon-\frac{Z-1}{r}-Z^{-2}r^{-3}\geqslant 0 \tag{3.14}$$

hold, and where

$$v(r_0)\geqslant\sqrt{\rho(r_0)}, \tag{3.15}$$

then theorem 1.1 implies $v(r)\geqslant\sqrt{\rho(r)}$ for all x with $r\geqslant r_0$.

By a straightforward but lengthy computation it can be shown that

$$v=C(1-s/r)r^{(Z-1)/\sqrt{2\epsilon}-1}\,\mathrm{e}^{-\sqrt{2\epsilon}r} \tag{3.16}$$

satisfies (3.13) provided

$$s>(Z-1)/(8\epsilon)[(Z-1)/\sqrt{2\epsilon}-1] \tag{3.17}$$

and

$$r_0\geqslant\max[s,(Z^{-2}+as-s)/(\sqrt{2\epsilon}-a^2/2+a/2)], \qquad a=(Z-1)/\sqrt{2\epsilon}. \tag{3.18}$$

If in addition

$$C\geqslant\sqrt{\rho(r_0)}(1-s/r_0)^{-1}r_0^{-a+1}\,\mathrm{e}^{\sqrt{2\epsilon}r_0}, \tag{3.19}$$

then v satisfies (3.15) and we obtain via theorem 1.1 the following upper bound to $\sqrt{\rho}$.

Theorem 3.1. Let r_0 satisfy the conditions (3.8), (3.14) and (3.18) and let s and C be defined according to (3.17) and (3.19); then

$$\sqrt{\rho(r)} \leq C(1-s/r)r^{(Z-1)/\sqrt{2\epsilon}-1}\,\mathrm{e}^{-\sqrt{2\epsilon}r}, \qquad \text{for } r \geq r_0. \tag{3.20}$$

Remark. Since $\sqrt{\rho(r_0)}$ can be estimated in terms of the upper bounds given by Hoffmann-Ostenhof and Hoffmann-Ostenhof (1978), (3.20) represents an explicit estimate for $\sqrt{\rho}$.

4. Discussion

Let us first comment on the lower bound given in theorem 2.1. Clearly only the δ in (2.11) prevents us from obtaining the exact asymptotic behaviour. The most natural thing to do to eliminate the δ would be to consider the differential equation

$$\left(-\frac{\Delta_1}{2}-\frac{Z}{r_1}+\epsilon\right)u_\infty+\int \phi_\infty(x_2)\psi(x_1, x_2)|x_1-x_2|^{-1}\,\mathrm{d}x_2=0. \tag{4.1}$$

However, we could not find a useful upper bound to the electronic repulsion term, and the δ is the price we have to pay for our decoupling of the inter-electronic repulsion.

Obviously theorem 2.1 can be extended to cover ground state densities of other two-electron systems with fixed nuclei like the hydrogen molecule. An extension to excited states and to many-electron systems is probably difficult, since some information on nodal properties of bound state functions seems to be necessary.

The asymptotic behaviour of the upper bound to $\rho(x)$ appears to be satisfactory. Let us give an interpretation to make its physical content clear. An electron far from the nucleus 'sees' the screened nucleus and needs a promotion energy ϵ to evade. This situation corresponds intuitively for very large r to

$$\left(-\frac{\Delta}{2}-\frac{Z-1}{r}+\epsilon\right)\sqrt{\rho}=0, \tag{4.2}$$

which has been replaced by the rigorous differential inequality (3.12).

That the proposed limiting behaviour

$$\rho(r) \sim kr^{2(Z-1)/\sqrt{2\epsilon}-2}\,\mathrm{e}^{-2\sqrt{2\epsilon}r} \tag{4.3}$$

is also of numerical interest has been demonstrated by Carlton (1979). He showed, partly motivated by the conjecture (4.3) (Hoffmann-Ostenhof and Hoffmann-Ostenhof 1977), that very accurately computed one-electron densities of helium-like atoms can be extremely well represented by a function $\tilde{\rho}=cr^m\,\mathrm{e}^{-2\sqrt{2\epsilon}r}$ with m close to $2(Z-1)/\sqrt{2\epsilon}-2$ in a region approximately given by $5<Zr<10$ (au). We do not expect that our upper bounds will be very good in this region, but certainly some refinements of our methods are possible since $F(x)$ can be calculated to any desired accuracy, although we do not know how inequality (3.5) affects our estimates.

Finally we remark that for the upper bound the restriction to the ground state density of two-electron atoms is not severe, but since there arise some new aspects for general many-electron systems we postpone a generalisation.

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