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A comparison theorem for differential inequalities with applications in quantum mechanics†

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Abstract. A theorem on differential inequalities is proved. By means of this theorem the following result is established. Let $\psi(r_1, r_2, r_{12})$ denote the ground-state wavefunction of a two-electron atom; then $\psi(r_1, r_2, r_{12}) \leqslant \psi(r_1, r_2, r'_{12})$ for $r'_{12} \geqslant r_{12}$. Furthermore, a different proof is given, for the hydrogenic molecular ion, of a recent result of Lieb and Simon on the monotonicity of the electronic part of the Born–Oppenheimer energy with respect to the internuclear distance.

1. Introduction

The usefulness of differential inequality techniques for obtaining rigorous results on bound-state wavefunctions has been noticed only recently (Simon 1975, Bardos and Merigot 1977, Morgan 1978, Hoffmann-Ostenhof *et al* 1978, Deift *et al* 1978, Hoffmann-Ostenhof 1979).

In this paper we shall derive a comparison theorem for differential inequalities which to our knowledge is new. This theorem will be applied to the ground-state wavefunction of helium-like systems and will also be used to provide an alternative proof of a result of Lieb and Simon (1978) on the electronic ground-state energy of the hydrogenic molecular ion.

To provide motivation, we first state a comparison theorem for differential inequalities which turned out to be very useful for the investigation of decay properties of atomic subcontinuum wavefunctions (Hoffmann-Ostenhof *et al* 1978, Deift *et al* 1978).

Theorem 1.1. Let Ω be an open subset of R^n. Suppose that the functions f and g satisfy the following conditions:

(i) $f, g \in C^0(\bar{\Omega})$ (continuous in the closure of Ω);
(ii) $f, g \to 0$ as $|x| \to \infty$ in Ω and $f, g \geqslant 0$ $\forall x \in \Omega$;
(iii) $f \geqslant g$ $\forall x \in \partial\Omega$;
(iv) $0 \leqslant V(x) \leqslant W(x)$ in Ω;
(v) $\left.\begin{matrix} \Delta f \leqslant Vf \\ \Delta g \geqslant Wg \end{matrix}\right\}$ in the distributional sense in Ω.

Then $f \geqslant g$ in all of Ω.

† Dedicated to Professor Oskar E Polansky on the occasion of his 60th birthday.

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The proof is based entirely on the maximum principle (see e.g. Deift *et al* 1978) and can be extended to cases where the Laplacian in (v) is replaced by a more general elliptic operator (Protter and Weinberger 1967).

The applicability of theorem 1.1 to many problems of interest is somewhat hampered by condition (iv), since (iv) implies that we can compare f with g only in those regions where g is subharmonic.

In § 2 we will overcome this restriction on V and W under some mild additional requirements on f and g. Section 3 will consist of the aforementioned applications.

2. Comparison theorems

Let Ω be an open, unbounded subset of R^n. We shall consider functions $\phi: \Omega \to R^1$ with the following properties:

(a) $\phi \in C^0(\bar{\Omega})$;

(b) $\phi \to 0$ as $|x| \to \infty$ in Ω;

(c) $\Delta\phi \in L^1(\Omega)$ $\quad (\int_\Omega |\Delta\phi|\, dx < \infty)$.

The following theorem is our main result.

Theorem 2.1. Let f and g satisfy the conditions (a)–(c). Furthermore let f and g have the following properties:

(i) $f > 0$ almost everywhere in Ω.

(ii) $f \geqslant g$ $\forall x \in \partial\Omega$.

(iii) $V(x) < W(x)$ almost everywhere in Ω.

(iv) $\left.\begin{matrix} \Delta f \leqslant Vf \\ \Delta g \geqslant Wg \end{matrix}\right\}$ in the distributional sense in Ω.

Then $f \geqslant g$ in all of Ω.

Proof. Let $D_d = \{x \in \Omega: g - f > d > 0\}$. Obviously D_d is, for every $d > 0$, a bounded subset of Ω. If we can show that D_d is empty for every $d > 0$ the theorem is proved. We shall give the proof in two steps. In step (1) we shall show that D_d is empty if $f, g \in C^\infty(\Omega)$ (the functions infinitely differentiable in Ω). In step (2) we complete the proof via regularisation.

Step (1). We assume that for sufficiently small d, D_d is non-empty. (i), (ii) and (iv) imply that, for $x \in D_d$, $f\Delta g - g\Delta f \geqslant (W - V)fg$ and from (iii) it follows that

$$\int_{D_d} (f\Delta g - g\Delta f)\, dx > 0, \tag{2.1}$$

where the integral is monotonically non-increasing in d. Now let $F = f + d/2$ and $G = g - d/2$; then

$$\int_{D_d} (F\Delta G - G\Delta F)\, dx = \int_{D_d} (f\Delta g - g\Delta f)\, dx + d/2 \int_{D_d} (\Delta f + \Delta g)\, dx. \tag{2.2}$$

Condition (c) implies

$$\left| \int_{D_d} (\Delta f + \Delta g)\, dx \right| \leqslant \int_\Omega (|\Delta f| + |\Delta g|)\, dx < \infty. \tag{2.3}$$

Therefore the right-hand side of (2.2) will be positive for sufficiently small d. Application of Green's formula to the left-hand side of (2.2) leads for sufficiently small d to

$$\int_{\partial D_d} F\boldsymbol{n}\nabla(G-F)\,\mathrm{d}x > 0, \tag{2.4}$$

since $F = G$ for $x \in \partial D_d$. $\boldsymbol{n}$ denotes the outward-directed unit normal vector. Since $F > 0$ there is a non-empty subset Γ of ∂D_d such that $\boldsymbol{n}\nabla(G-F) > 0\ \forall x \in \Gamma$. This implies that the inward-directed normal derivative is negative for $x \in \Gamma$, and hence that there are points in D_d with $G - F < 0$ which in turn implies $g - f < d$. Therefore D_d is empty for every $d > 0$.

Step (2). Let $\rho(x)$ be a non-negative function belonging to $C_0^\infty(R^n)$ (the infinitely differentiable functions with compact support), with the properties $\rho(x) = 0$ if $x \geqslant 1$ and $\int \rho(x)\,\mathrm{d}x = 1$. Let $\delta > 0$ and let ϕ satisfy the conditions (a)–(c) and

$$\phi_\delta = \delta^{-n} \int_{D_{d/2}} \rho\left(\frac{x-y}{\delta}\right)\phi(y)\,\mathrm{d}y. \tag{2.5}$$

Now let $D_d^\delta = \{x \in D_{d/2} : g_\delta - f_\delta > d\}$ First we note two properties of ϕ which we will need:

(A) $\phi_\delta \to \phi$ uniformly as $\delta \to 0$ in $D_{d/2}$;

(B) $\int_{D_{d/2}} |\Delta(\phi_\delta - \phi)|\,\mathrm{d}x \to 0$ as $\delta \to 0$.

For a proof of these two properties see for instance Gilbarg and Trudinger (1977).

We assume again that for sufficiently small d, D_d is non-empty. (A) implies that D_d^δ is also non-empty for sufficiently small δ and we shall establish a contradiction as in step (1).

Let $F_\delta = f_\delta + d/2$, $G_\delta = g_\delta - d/2$. As in step (1) we have

$$\int_{D_d^\delta} (F\Delta G - G\Delta F)\,\mathrm{d}x > 0 \tag{2.6}$$

for sufficiently small δ. Now

$$\left|\int_{D_d^\delta} (F_\delta \Delta G_\delta - G_\delta \Delta F_\delta)\,\mathrm{d}x - \int_{D_d^\delta} (F\Delta G - G\Delta F)\,\mathrm{d}x\right|$$

$$\leqslant \int_{D_d^\delta} |F_\delta \Delta G_\delta - F\Delta G|\mathrm{d}x + \int_{D_d^\delta} |G_\delta \Delta F_\delta - G\Delta F|\,\mathrm{d}x. \tag{2.7}$$

For δ sufficiently small, (A, B) implies $D_d^\delta \subset D_{d/2}$ and, for $\delta \to 0$,

$$\int_{D_d^\delta} |F_\delta \Delta G_\delta - F\Delta G|\,\mathrm{d}x$$

$$\leqslant \sup_{x \in D_{d/2}} |f_\delta - F| \int_{D_{d/2}} |\Delta g|\,\mathrm{d}x + \sup_{x \in D_{d/2}} |F_\delta| \int_{D_{d/2}} |\Delta(g - g_\delta)|\,\mathrm{d}x \to 0. \tag{2.8}$$

This implies that the right-hand side of (2.7) vanishes as $\delta \to 0$, which together with (2.6) leads for sufficiently small δ to

$$\int_{D_d^\delta} (F_\delta \Delta G_\delta - G_\delta \Delta F_\delta)\,\mathrm{d}x > 0. \tag{2.9}$$

By application of Green's formula we obtain, in agreement with the reasoning in step (1), the desired contradiction.

Remark 2.1
Theorem 2.1 obviously holds also if Ω is a bounded set. In this case it can also be proved by applying Hopf's maximum principle to g/f in the spirit of the methods given in the book of Protter and Weinberger (1967).

The Laplacian in condition (iv) can be replaced by a more general elliptic operator in divergence form. We state here this extension of theorem 2.1 and only indicate its proof. Let $A(x)$ be a matrix function defined on $\Omega \subset R^n$:

$$A(x) = \begin{pmatrix} a_{11}(x) & a_{12}(x) & \dots & a_{1n}(x) \\ & \ddots & & \\ a_{n1}(x) & a_{n2}(x) & \dots & a_{nn}(x) \end{pmatrix}$$

with $x = (x_1, x_2, \dots, x_n) \in R^n$ and $a_{ij}(x)$ continuously differentiable, $\forall x \in \bar{\Omega}$. We also assume that, as a matrix, A is symmetric and positive definite, i.e. its lowest eigenvalue is strictly positive $\forall x \in \Omega$. In the following the operator $\nabla = (\partial/\partial x_1, \partial/\partial x_2, \dots, \partial/\partial x_n)$ is to be understood as a vector operator acting, depending on the situation, as row or as column vector.

Theorem 2.2. Suppose f and g satisfy the conditions (a) and (b) and that (c) is replaced by

(c') $\quad \nabla(A\nabla\phi) \in L^1(\bar{\Omega})$.

Furthermore f and g should satisfy (i)–(iii) of theorem 2.1 and (iv) be replaced by

$$\text{(iv')} \qquad \left.\begin{aligned} \nabla(A\nabla f) &\leqslant Vf \\ \nabla(A\nabla g) &\geqslant Wg \end{aligned}\right\} \text{ in the distributional sense in } \Omega. \tag{2.10}$$

Then $f \geqslant g$ in all of Ω.

Sketch of the proof. We only reconsider step (1). We have, for f and g belonging to $C^\infty(\Omega)$,

$$f\nabla(A\nabla g) = \nabla(fA\nabla g) - (\nabla f)A(\nabla g). \tag{2.11}$$

The last term on the right-hand side of equation (2.11) should be understood in the sense that (∇f) denotes a row vector and (∇g) a column vector. For simplicity we assume that $\partial\Omega$ is sufficiently smooth and consider only $D_0 = \{x \in \Omega : g - f > 0\}$. From (2.10) and (2.11) we have in D_0

$$f\nabla(A\nabla g) - g\nabla(A\nabla f) \geqslant (W - V)fg \tag{2.12}$$

and

$$\nabla(fA\nabla g) - \nabla(gA\nabla f) \geqslant 0. \tag{2.13}$$

Hence Green's formula leads to

$$\int_{D_0} \nabla(fA\nabla g - gA\nabla f)\, \mathrm{d}x = \int_{\partial D_0} nfA(\nabla g - \nabla f)\, \mathrm{d}\sigma > 0, \tag{2.14}$$

where we used the fact that A is a symmetric matrix. The positive definiteness of A implies $\boldsymbol{nAn} > 0$. This in turn implies that $\boldsymbol{An}$ is an outward-directed vector for $x \in \partial D_0$ and hence we have $\boldsymbol{\nabla}(g-f)\boldsymbol{An} > 0$ on a non-empty subset of ∂D_0. This leads, in complete analogy to the previous case, to a contradiction implying that D_0 is empty.

Step (2) leads to no new complications and will be omitted here.

Remark 2.2. We shall not apply theorem 2.2 in the next section. However, it should be noted that it seems to be very useful for the investigation of asymptotic properties of bound-state eigenfunctions of general many-particle Hamiltonians with centre of gravity removed, since for such Hamiltonians the usual Laplacian is replaced by an operator $\boldsymbol{\nabla} A \boldsymbol{\nabla}$ with A a constant matrix.

We shall now apply theorem 2.1 to eigenvalue problems. (Analogous results can be also derived from theorem 2.2.)

Theorem 2.3. Suppose $\psi(x_1, x_2, \ldots, x_n)$ is a bound-state solution of the Schrödinger equation (the corresponding Hamiltonian is defined on $L^2(R^n)$)

$$-\Delta\psi + (U(x_1, x_2, \ldots, x_n) - E)\psi = 0, \tag{2.15}$$

E being the ground-state energy. The potential U is assumed to be sufficiently smooth such that ψ satisfies the conditions (a)–(c) and $\psi > 0$ almost everywhere. If $U(x_1, x_2, \ldots, x_n) < U(-x_1, x_2, \ldots, x_n)$ for all $x_1 > 0$, then $\psi(x_1, x_2, \ldots, x_n) \geqslant \psi(-x_1, x_2, \ldots, x_n)$ $\forall x_1 > 0$.

Remark 2.3.. For most potentials of physical interest (see Reed and Simon 1978) the mathematical ground state (i.e. no symmetry restrictions) is almost everywhere positive.

Proof. This is a straightforward application of theorem 2.1. Let $\Omega = \{x \in R^n : x_1 > 0\}$. In Ω we define the following functions: $f = \psi(x_1, \ldots, x_n)$, $g = \psi(-x_1, \ldots, x_n)$, $V = U(x_1, \ldots, x_n) - E$ and $W = U(-x_1, \ldots, x_n) - E$. For $x_1 > 0$ we have $\Delta f = Vf$ and $\Delta g = Wg$. Since $f = g$ for $x \in \partial\Omega$ we can apply theorem 2.1 to conclude that $f \geqslant g$ for $x_1 > 0$.

Remark 2.4. A closely related theorem has been proved by Lieb and Simon (1978) by completely different methods.

3. Applications

We shall first apply theorem 2.3 to the helium ground-state wavefunction. We consider a fixed nucleus with nuclear charge Z and two electrons. The Hamiltonian is given by

$$H = -\tfrac{1}{2}(\partial/\partial x_1^2 + \partial/\partial x_2^2 + \partial/\partial x_3^2 + \partial/\partial y_1^2 + \partial/\partial y_2^2 + \partial/\partial y_3^2) - Z(x_1^2 + x_2^2 + x_3^2)^{-1/2} - Z(y_1^2 + y_2^2 + y_3^2)^{-1/2} + [(x_1 - y_1)^2 + (x_2 - y_2)^2 + (x_3 - y_3)^2]^{-1/2}, \tag{3.1}$$

where $x = (x_1, x_2, x_3)$ and $y = (y_1, y_2, y_3)$ denote the positions of the electrons in R^3. We adopt the usual abbreviations $r_1 = |x|$, $r_2 = |y|$, $r_{12} = |x - y|$. It is well known that the ground state ψ depends only on r_1, r_2 and r_{12} and is symmetric with respect to permutation of the electron coordinates, i.e. $\psi(x, y) = \psi(y, x)$ (Hylleraas 1964).

Theorem 3.1. Let $\psi(r_1, r_2, r_{12})$ be the ground state of a two-electron atom described by the Hamiltonian (3.1); then

$$\psi(r_1, r_2, r_{12}) \geqslant \psi(r_1, r_2, r'_{12}) \tag{3.2}$$

for $r'_{12} \leqslant r_{12}$.

Proof. First we note that ψ is continuous (Kato 1957) and almost everywhere positive (Reed and Simon 1978). Furthermore since for suitable $\alpha > 0$, $C > 0$,

$$\psi(x, y) \leqslant C \exp(-\alpha r_1 - \alpha r_2) \tag{3.3}$$

(see e.g. Deift *et al* (1978)), we obtain

$$\begin{aligned} \int |\Delta\psi| \, dx \, dy &= 2 \int |(-Z/r_1 - Z/r_2 + 1/r_{12} - E)\psi| \, dx \, dy \\ &\leqslant 2C \int (Z/r_1 + Z/r_2 + 1/r_{12} + |E|) \exp(-\alpha r_1 - \alpha r_2) \, dx \, dy < \infty \end{aligned} \tag{3.4}$$

as can be seen from some obvious estimates. Hence ψ satisfies the conditions (a)–(c) of § 2.

Now let

$$\Omega_1 = \{(x, y): x_1 > 0, y_1 < 0\}, \qquad \Omega_2 = \{(x, y): x_1 < 0, y_1 > 0\} \quad \text{and} \quad \Omega = \Omega_1 \cup \Omega_2.$$

The potential U,

$$U = -Z/r_1 - Z/r_2 + 1/r_{12}, \tag{3.5}$$

satisfies the following inequalities in Ω:

$$\begin{aligned} U(x_1, x_2, x_3, y_1, y_2, y_3) &< U(-x_1, x_2, x_3, y_1, y_2, y_3), \\ U(x_1, x_2, x_3, y_1, y_2, y_3) &< U(x_1, x_2, x_3, -y_1, y_2, y_3). \end{aligned} \tag{3.6}$$

We now rename our functions:

$$V(x_1, x_2, x_3, y_1, y_2, y_3) = U - E \text{ for } (x, y) \in \Omega,$$

$$W(x_1, x_2, x_3, y_1, y_2, y_3) = \begin{cases} U(-x_1, x_2, x_3, y_1, y_2, y_3) - E & \text{for } (x, y) \in \Omega_1 \\ U(x_1, x_2, x_3, -y_1, y_2, y_3) - E & \text{for } (x, y) \in \Omega_2, \end{cases} \tag{3.7}$$

and

$$f(x_1, x_2, x_3, y_1, y_2, y_3) = \psi(x, y) \quad \text{for } (x, y) \in \Omega,$$

$$g(x_1, x_2, x_3, y_1, y_2, y_3) = \begin{cases} \psi(-x_1, x_2, x_3, y_1, y_2, y_3) & \text{for } (x, y) \in \Omega_1 \\ \psi(x_1, x_2, x_3, -y_1, y_2, y_3) & \text{for } (x, y) \in \Omega_2. \end{cases} \tag{3.8}$$

For $(x, y) \in \partial\Omega$ we have $f = g$ since the symmetry behaviour of ψ implies

$$\psi(0, x_2, x_3, y_1, y_2, y_3) = \psi(0, x_2, x_3, -y_1, y_2, y_3)$$

and

$$\psi(x_1, x_2, x_3, 0, y_2, y_3) = \psi(-x_1, x_2, 0, y_1, y_2, y_3).$$

Hence we obtain for $(x, y) \in \Omega$, $\Delta f = 2Vf$ and $\Delta g = 2Wg$. Therefore theorem 2.1 implies $f \geqslant g$ or, for $(x, y) \in \Omega$,

$$\psi(x, y) \geqslant \psi(-x_1, x_2, x_3, y_1, y_2, y_3)$$

and

$$\psi(x, y) \geqslant \psi(x_1, x_2, x_3, -y_1, y_2, y_3).$$

The symmetry properties of ψ now imply (3.2).

Remark 3.1. Theorem 2.3 and the result given in theorem 3.1 can be easily interpreted on physical grounds. One expects that the wavefunction should be in some sense small if the potential is large and vice versa. This vague feeling is made precise by those theorems though the situations which can be handled are admittedly very special.

Remark 3.2. (3.2) can be written also in a different form, which is perhaps more transparent, by introducing the angle θ between the two vectors x and y. The result reads then $\psi(r_1, r_2, \theta) \geqslant \psi(r_1, r_2, \theta')$ for $\theta \geqslant \theta'$, $0 \leqslant \theta \leqslant \pi$. This clearly describes the angular correlation of ψ.

Remark 3.3. A similar result can be also obtained for the ground state of the hydrogen molecule described by a Hamiltonian with fixed nuclei. Let $\psi(r_1, r_2, r_1', r_2', \theta)$ denote the electronic ground state of this molecule, where r_1 and r_2 denote the distances of the first electron from the two fixed nuclei and r_1', r_2' denote the distances of the second electron. θ denotes the angle between the two triangles built up by the two nuclei and the first and the second electron respectively. In complete analogy to the treatment of the helium problem we obtain $\psi(r_1, r_2, r_1', r_2', \theta) \geqslant \psi(r_1, r_2, r_1', r_2', \theta')$ for $\theta \geqslant \theta'$ and $0 \leqslant \theta \leqslant \pi$.

Finally we consider the electronic ground-state energy $e(R)$ of the hydrogenic molecular ion. This system is described by the following Hamiltonian, where R denotes the distance of the two nuclei with charge Z:

$$H = -\tfrac{1}{2}(\partial^2/\partial x^2 + \partial^2/\partial y^2 + \partial^2/\partial z^2) - Z(x^2+y^2+z^2)^{-1/2} - Z((x-R)^2+y^2+z^2)^{-1/2}. \tag{3.9}$$

We consider the corresponding Schrödinger equation $H\psi = e(R)\psi$, with H and ψ depending parametrically upon R. Lieb and Simon (1978) proved the following result:

Theorem 3.2. $e(R)$ is monotonically non-decreasing.

Sketch of the proof. This is a straightforward consequence of theorem 2.3 and will be only indicated, since one of the two proofs of Lieb and Simon (1978) is based on a theorem closely related to theorem 2.3.

The Hellmann–Feynman theorem implies that

$$\mathrm{d}e/\mathrm{d}R = Z \int \psi(x, y, z)^2 (R-x)((x-R)^2+y^2+z^2)^{-3/2}\, \mathrm{d}x\, \mathrm{d}y\, \mathrm{d}z. \tag{3.10}$$

This expression can be transformed via a variable transformation into

$$\mathrm{d}e/\mathrm{d}R = \int \mathrm{d}y \int \mathrm{d}z \int_R^\infty \mathrm{d}x (x-R)((x-R)^2+y^2+z^2)^{-3/2}(\psi(2R-x, y, z)^2 - \psi(x, y, z)^2). \tag{3.11}$$

Theorem 2.3 obviously also holds if the origin is shifted, that is to say, in our example, if for $x > R$, $U(x, y, z) > U(2R-x, y, z)$ then $\psi(x, y, z) \leqslant \psi(2R-x, y, z)$ for $x > R$. A closer inspection of the potential in (3.9) shows that this is indeed the case. This in turn implies the positivity of the integral in (3.11) and hence the monotonicity of $e(R)$.

Remark 3.4. To prove theorem 3.2, local properties of the wavefunction were used to obtain results on the energy. However, in order to extend this result to one-electron systems with n nuclei ($n > 2$) other methods appear to be necessary, as has been demonstrated by Lieb and Simon (1978).

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