Lower bounds for quantum mechanical energy levels

1978 J. Phys. A: Math. Gen. 11 55

(http://iopscience.iop.org/0305-4470/11/1/009)

J. Phys. A: Math. Gen., Vol. 11, No. 1, 1978. Printed in Great Britain.

Lower bounds for quantum mechanical energy levels

Michael F Barnsley†

Department of Mathematics, University of Bradford, Bradford BD7 1DP, UK
and
Centre d'Etudes Nucléaires de Saclay, Service de Physique Atomique, BP No. 2,91190 Gif-sur-Yvette, France

Received 13 June 1977, in final form 1 September 1977

Abstract. The application of Barta's method to Schrödinger's equation is reviewed, the result of Duffin being extended in several directions.

1. Introduction

Duffin (1947) has given an interesting method for finding lower bounds for the ground state eigenvalue of Schrödinger's equation. His method is an extension of one due to Barta (1937) for approximating the fundamental frequency of a vibrating membrane. Although the method is well known to specialists in the area of uniform elliptic differential operators (see the references given in the next section) it has been largely overlooked by workers in quantum mechanics. The method is closely related to the 'local energy' method (see for example Frost 1942, Bartlett 1955, Bethe and Salpeter 1957, Stanton and Taylor 1966) yet the author has been able to find no reference to it in this context.

In this paper we review the application of Barta's method to Schrödinger's equation, and extend the result of Duffin in several directions. This is achieved in a sequence of theorems, some essentially those of other workers and some of them new. The usage of the method is illustrated with simple examples, including the determination of a lower bound for the ground state energy of H_2^+ as a function of the distance between the nuclei.

We do not claim that the method as it stands will straightforwardly produce lower bounds of high quality in the majority of problems encountered by theoretical chemists. For example, in the case of systems involving more than two electrons the method provides a lower bound to the unphysical ground state energy which is obtained when the antisymmetry constraint on the wavefunction is ignored. Nonetheless we believe that a knowledge of the method adds to the understanding of the quantum mechanical eigenvalue problem and may well lead to useful developments.

† Present address: Centre d'Etudes Nucléaires de Saclay, Service de Physique Théorique, BP No. 2,91190 Gif-sur-Yvette, France.

2. One-dimensional problems

2.1. Problems posed on a finite interval

Here we consider the situation typified by a particle of mass m which moves one-dimensionally on the x axis in a real potential $V(x)$ such that

$$V(x) \text{ is } \begin{cases} \text{continuous for } x \in [a, b] \text{ where } -\infty < a < b < +\infty, \\ \text{positive infinite for } x \notin [a, b]. \end{cases} \tag{2.1.1}$$

The corresponding Schrödinger wave equation for stationary bound states is, in atomic units,

$$H\psi(x) = -\frac{1}{2m}\frac{d^2}{dx^2}\psi(x) + V(x)\psi(x) = E\psi(x), \qquad x \in [a, b], \tag{2.1.2}$$

with the boundary conditions

$$\psi(a) = \psi(b) = 0. \tag{2.1.3}$$

The real number E is an energy eigenvalue, and any wavefunction $\psi(x)$ belonging to E is required not to vanish identically over $[a, b]$.

Discussion of the above problem is simplified because one knows *a priori* the following results; see for example Birkhoff and Rota (1962). The system has an infinite sequence of real eigenvalues $E_0 < E_1 < E_2 < \ldots$ with $\lim_{n\to\infty} E_n = \infty$. The eigenfunction $\psi_n(x)$ belonging to the eigenvalue E_n possesses a continuous second derivative on $[a, b]$, has exactly n zeros in the interval $a < x < b$, and is uniquely determined up to a constant factor.

The central idea behind the results in this paper is exemplified by the following theorem, various forms of which have previously been given by Barta (1937), Duffin (1947), Fichera (1954), Hersch (1959), Protter and Weinberger (1967), and others. The theorem was substantially known by Picard (1893) and Boggio (1907).

Theorem 1. For $x \in [a, b]$ let $\Psi(x)$ be any function, not identically zero, such that $\Psi''(x)$ exists and is continuous, such that $\Psi(x) \geqslant 0$, and such that

$$\Psi(a) \geqslant 0 \qquad \text{and} \qquad \Psi(b) \geqslant 0. \tag{2.1.4}$$

Then

$$\text{Inf}\left(\frac{H\Psi(x)}{\Psi(x)} : x \in [a, b], \Psi(x) \neq 0\right) \leqslant E_0 \tag{2.1.5}$$

where E_0 is the lowest eigenvalue of the problem (2.1.2) and (2.1.3).

Proof. Let

$$\gamma = \min(H\Psi(x) - E_0\Psi(x) : x \in [a, b]). \tag{2.1.6}$$

Then because $H\Psi(x) - E_0\Psi(x)$ is continuous for $x \in [a, b]$ we have that γ is finite and there exists $x_0 \in [a, b]$ such that

$$\gamma = H\Psi(x_0) - E_0\Psi(x_0). \tag{2.1.7}$$

We consider separately the two possibilities

$$\text{(i) } \gamma < 0, \qquad \text{and} \qquad \text{(ii) } \gamma \geqslant 0. \tag{2.1.8}$$

If (i) is true then the continuity of $H\Psi(x)-E_0\Psi(x)$ implies that there exists an open neighbourhood $N(x_0)$ of x_0 such that

$$H\Psi(x)-E_0\Psi(x)<0 \qquad \text{for all } x\in[a,b]\cap N(x_0), \tag{2.1.9}$$

and in particular $\Psi(x)$ cannot vanish identically on any open subinterval contained in $[a,b]\cap N(x_0)$. Hence $\Psi(x)$ can vanish only at isolated points in $[a,b]\cap N(x_0)$ and it follows that

$$\Psi(x_1)>0 \qquad \text{for some } x_1\in[a,b]\cap N(x_0). \tag{2.1.10}$$

From (2.1.9) and (2.1.10) we obtain

$$H\Psi(x_1)/\Psi(x_1)<E_0 \tag{2.1.11}$$

which proves the proposition in case (i).

If (ii) is true then we have

$$H\Psi(x)-E_0\Psi(x)\geqslant 0 \qquad \text{for all } x\in[a,b]. \tag{2.1.12}$$

If the equality sign here pertains throughout the interval then

$$H\Psi(x)/\Psi(x)=E_0 \qquad \text{for all } x\in[a,b] \text{ such that } \Psi(x)\neq 0, \tag{2.1.13}$$

and the theorem follows. If the equality sign in (2.1.12) does not hold throughout the interval then, using continuity, there must exist some subinterval $[c,d]\subset[a,b]$ with $c<d$ such that

$$H\Psi(x)-E_0\Psi(x)\begin{cases}\geqslant 0 & \text{for all } x\in[a,b],\\ >0 & \text{for all } x\in[c,d].\end{cases} \tag{2.1.14}$$

Let us assume (2.1.14) is true. Then we note that

$$H\psi_0(x)-E_0\psi_0(x)=0 \qquad \text{for all } x\in[a,b], \tag{2.1.15}$$

where we can suppose $\psi_0(x)>0$ for all $x\in(a,b)$. Multiplying (2.1.14) by $\psi_0(x)$, (2.1.15) by $\Psi(x)$, and taking the difference we obtain

$$-\frac{\mathrm{d}}{\mathrm{d}x}\left(\psi_0(x)\frac{\mathrm{d}}{\mathrm{d}x}\Psi(x)-\Psi(x)\frac{\mathrm{d}}{\mathrm{d}x}\psi_0(x)\right)\begin{cases}\geqslant 0 & \text{for all } x\in[a,b],\\ >0 & \text{for all } x\in[c,d].\end{cases} \tag{2.1.16}$$

The latter quantity is continuous and so we can integrate over $[a,b]$, yielding

$$\left[-\psi_0(x)\frac{\mathrm{d}}{\mathrm{d}x}\Psi(x)+\Psi(x)\frac{\mathrm{d}}{\mathrm{d}x}\psi_0(x)\right]_a^b>0. \tag{2.1.17}$$

This is impossible in view of (2.1.4) and the fact that $\psi_0'(a)>0$ while $\psi_0'(b)<0$. We conclude that (2.1.14) is false.

The above proposition says that for some $x\in[a,b]$ the 'local energy' $E(x)=H\Psi(x)/\Psi(x)$ is less than or equal to the true ground state energy E_0 when Ψ is a sensible approximation to ψ_0. This result is complementary to the Rayleigh–Ritz bound

$$E_0\leqslant\frac{\int_a^b\Psi(x)H\Psi(x)\,\mathrm{d}x}{\int_a^b\Psi(x)\Psi(x)\,\mathrm{d}x} \tag{2.1.18}$$

which applies when Ψ satisfies the boundary conditions. The similarity in appearance between the expectation value in (2.1.18) and the lower bound in (2.1.5) is striking.

We will later see that theorem 1 extends to the case of far more general quantum mechanical systems. However, a unique feature of one-dimensional problems is that a similar theorem applies to excited states.

Theorem 2. For $x \in [a, b]$ let $\Psi_n(x)$ be any real function vanishing only at isolated points, such that $\Psi_n''(x)$ exists and is continuous, and such that $\Psi_n(x)$ changes sign exactly n times as x progresses from a to b. Furthermore let $\Psi_n(x)$ be non-negative throughout some neighbourhood of a, with

$$\Psi_n(a) \geqslant 0, \qquad \text{and} \qquad (-1)^n \Psi_n(b) \geqslant 0. \tag{2.1.19}$$

Then

$$\operatorname{Inf}\left(\frac{H\Psi_n(x)}{\Psi_n(x)}: x \in [a, b], \Psi(x) \neq 0\right) \leqslant E_n, \qquad n = 0, 1, 2, \ldots \tag{2.1.20}$$

where E_n is the $(n+1)$th eigenvalue of the problem (2.1.2) and (2.1.3).

Proof. We know that $\psi_n(x)$ has precisely n zeros in the interval $a < x < b$. Let us denote the locations of these zeros by $x_j^{(n)}$, $j = 1, 2, \ldots, n$, where

$$a < x_1^{(n)} < x_2^{(n)} < \ldots < x_n^{(n)} < b. \tag{2.1.21}$$

Then setting $x_0^{(n)} = a$ and $x_{n+1}^{(n)} = b$ we consider the following $(n+1)$ different eigenvalue problems:

$$\left.\begin{aligned} &H\psi(x) = E\psi(x), \qquad x \in [x_i^{(n)}, x_{i+1}^{(n)}] \\ &\psi(x_i^{(n)}) = \psi(x_{i+1}^{(n)}) = 0, \end{aligned}\right\} \qquad i = 0, 1, \ldots, n. \tag{2.1.22}$$

The eigenfunction $\psi_n(x)$ (with x lying in the appropriate interval) satisfies each of the above problems with $E = E_n$. Moreover $\psi_n(x)$ has no zeros for x restricted to any one of the domains $a < x < x_1^{(n)}$, $x_1^{(n)} < x < x_2^{(n)}, \ldots, x_n^{(n)} < x < b$. It follows that E_n is the lowest eigenvalue for each of the above problems. Since $\Psi_n(x)$ changes sign n times on $[a, b]$ it follows that it does not change sign throughout at least one of the $(n+1)$ intervals $[x_i^{(n)}, x_{i+1}^{(n)}]$, $i = 0, 1, \ldots, n$. Let such an interval be $[x_k^{(n)}, x_{k+1}^{(n)}]$. Since $\Psi_n(x)$ does not change sign on $[x_k^{(n)}, x_{k+1}^{(n)}]$ and does not vanish identically on this interval (its zeros being isolated), we can apply theorem 1 to the $(k+1)$th eigenvalue problem in (2.1.22) with $\Psi(x) = (-1)^k \Psi_n(x)$, yielding

$$\operatorname{Inf}\left(\frac{H\Psi_n(x)}{\Psi_n(x)}: x \in [x_k^{(n)}, x_{k+1}^{(n)}], \Psi_n(x) \neq 0\right) \leqslant E_n, \tag{2.1.23}$$

which implies (2.1.20).

A result along similar lines to the above has been given by Redheffer (1966).

Example 1. We use theorem 2 to derive some bounds given by Breuer and Gottlieb (1971). Let $\tilde{E}_0 < \tilde{E}_1 < \tilde{E}_2 \ldots$ and $\tilde{\psi}_0, \tilde{\psi}_1, \tilde{\psi}_2, \ldots$ denote respectively the eigenvalues and eigenfunctions belonging to the problem (2.1.2) and (2.1.3) when $V(x)$ is replaced by a different continuous function $\tilde{V}(x)$. Then we can choose $\Psi_n(x) = \tilde{\psi}_n(x)$ in theorem 2, yielding

$$\tilde{E}_n + \min(V(x) - \tilde{V}(x): x \in [a, b]) \leqslant E_n. \tag{2.1.24}$$

Since the same relation must hold when E_n and V are interchanged with $\tilde{E}_n$ and $\tilde{V}$, it now follows that

$$\min(\tilde{V}(x)-V(x): x\in[a,b])\leqslant \tilde{E}_n - E_n \leqslant \max(\tilde{V}(x)-V(x): x\in[a,b]). \tag{2.1.25}$$

This result provides a simple measure of the error produced in the eigenvalues when a given potential is approximated by another which may be easier to work with.

Example 2. Consider the standard 'particle-in-a-box' eigenvalue problem

$$-\frac{1}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi(x)=E\psi(x); \qquad \psi(0)=\psi(1)=0 \tag{2.1.26}$$

for which we have the exact quantities

$$\psi_n(x)=\sin(n+1)\pi x, \qquad E_n=(n+1)^2\pi^2/2m, \qquad n=0,1,2,\ldots. \tag{2.1.27}$$

Then in (2.1.20) we can choose

$$\Psi_0(x)=x(1-x), \qquad \Psi_1(x)=x(1-2x)(1-x), \qquad \text{and} \qquad \Psi_1(x)=(1-2x)\sin\pi x, \tag{2.1.28}$$

which leads respectively to the lower bounds

$$8/2m\leqslant E_0, \qquad 24/2m\leqslant E_1, \qquad \text{and} \qquad 3\pi^2/2m\leqslant E_1. \tag{2.1.29}$$

We note that although these bounds are sensible, they are significantly less close to the exact values than the corresponding upper bounds which are obtained via the Rayleigh–Ritz method using exactly the same trial functions. For example, using the first two trial functions in (2.1.28) we find

$$E_0\leqslant 10/2m, \qquad \text{and} \qquad E_1\leqslant 42/2m, \tag{2.1.30}$$

which are better by factors of 13, and 7, respectively than their couterparts in (2.1.29).

Alternatively in this example we can choose

$$\Psi_n(x)=\sin\eta_n x \tag{2.1.31}$$

where η_n is a real parameter such that

$$n\pi<\eta_n\leqslant(n+1)\pi, \qquad n=0,1,2,\ldots. \tag{2.1.32}$$

Then we find the lower bounds

$$\eta_n^2/2m\leqslant E_n, \qquad n=0,1,2,\ldots. \tag{2.1.33}$$

These bounds approach the exact values smoothly as the trial functions approach the exact eigenfunctions at $\eta_n=(n+1)\pi$. We note that the trial functions do not satisfy the exact boundary conditions except when $\eta_n=(n+1)\pi$.

2.2. *$V(x)$ continuous for all x*

Here, unlike the situation in § 2.1, we are not assured of the existence of even a single bound state nor do we know how many nodes a given bound state wavefunction posseses. Thus, corresponding provisions have to be made in the statements of theorems.

A proposition similar to the following one has been given by Duffin (1947) who makes certain assumptions which we avoid by using a different proof.

Theorem 3. Let the real function $\psi(x)$, not identically zero but tending to zero as x tends to infinity, be continuous for all $x \in \mathbb{R}$, and satisfy

$$H\psi(x) = -\frac{1}{2m}\frac{d^2}{dx^2}\psi(x) + V(x)\psi(x) = E\psi(x), \qquad \text{for all } x \in \mathbb{R} \tag{2.2.1}$$

for some $E \in \mathbb{R}$. $V(x)$ is real and continuous with $(E - V(x)) < 0$ for all sufficiently large $|x|$. Let $\Psi(x)$ be any real function, vanishing only at isolated points, which undergoes no change of sign and is such that $H\Psi(x)$ is defined and continuous for all $x \in \mathbb{R}$. Then

$$\text{Inf}\left(\frac{H\Psi(x)}{\Psi(x)} : x \in \mathbb{R}, \Psi(x) \neq 0\right) \leq E. \tag{2.2.2}$$

Proof. Without any loss of generality we can assume that $\psi(c) = 1$ for some finite $c \in \mathbb{R}$. Let (a, b) be the largest real open interval containing c such that $\psi(x) \neq 0$ for all $x \in (a, b)$, where we may have $a = -\infty$, or $b = +\infty$, or both. Let $0 < \epsilon < 1$ be given, and let $(a(\epsilon), b(\epsilon))$ be the largest open interval contained in (a, b) such that

$$\psi(a(\epsilon)) = \psi(b(\epsilon)) = \epsilon. \tag{2.2.3}$$

Then it is clear that both $a(\epsilon)$ and $b(\epsilon)$ are finite and that $a(\epsilon) < b(\epsilon)$. Now let E_0^ϵ denote the least eigenvalue for the problem

$$H\phi(x) = -\frac{1}{2m}\frac{d^2}{dx^2}\phi(x) + V(x)\phi(x) = E^\epsilon\phi(x), \qquad x \in [a(\epsilon), b(\epsilon)], \tag{2.2.4}$$

where the boundary conditions are

$$\phi(a(\epsilon)) = \phi(b(\epsilon)) = 0. \tag{2.2.5}$$

Then on applying theorem 1 to this problem with $\Psi(x)$ as above we obtain

$$\text{Inf}\left(\frac{H\Psi(x)}{\Psi(x)} : x \in [a(\epsilon), b(\epsilon)], \Psi(x) \neq 0\right) \leq E_0^\epsilon. \tag{2.2.6}$$

The proof is completed if we show that E_0^ϵ tends to a value less than or equal to E as ϵ tends to zero. To this end we examine the Rayleigh–Ritz bound

$$E_0^\epsilon \leq \frac{\int_{a(\epsilon)}^{b(\epsilon)} \Phi(x) H\Phi(x)\, dx}{\int_{a(\epsilon)}^{b(\epsilon)} \Phi(x)^2\, dx}, \tag{2.2.7}$$

which is valid for all $\Phi(x)$ which vanish at $x = a(\epsilon)$ and $x = b(\epsilon)$, are not identically zero, and are such that $H\Phi(x)$ is continuous for all $x \in [a(\epsilon), b(\epsilon)]$. An admissible choice is

$$\Phi(x) = \psi(x) - \epsilon, \tag{2.2.8}$$

and this leads to

$$E_0^\epsilon \leq E + \frac{\epsilon \int_{a(\epsilon)}^{b(\epsilon)} (\psi(x) - \epsilon)(E - V(x))\, dx}{\int_{a(\epsilon)}^{b(\epsilon)} (\psi(x) - \epsilon)^2\, dx}. \tag{2.2.9}$$

Since $(E - V(x)) < 0$ whenever $|x| > M$ for some finite $M > 0$, and since $(\psi(x) - \epsilon) > 0$

for all $x \in [a(\epsilon), b(\epsilon)]$ when ϵ is sufficiently small, we now have for fixed $\tilde{\epsilon}$

$$E_0^{\epsilon} \leqslant E + \frac{\epsilon \int_{-M}^{+M} |\psi(x)||E - V(x)|\,\mathrm{d}x}{\int_{a(\tilde{\epsilon})}^{b(\tilde{\epsilon})} (\psi(x) - \tilde{\epsilon})^2\,\mathrm{d}x} \tag{2.2.10}$$

for all sufficiently small $\epsilon > 0$. The second term on the right-hand side here tends to zero as ϵ tends to zero so that either $\lim_{\epsilon \to 0} E_0^{\epsilon} = E$, or else $E_0^{\epsilon} < E$ whenever ϵ is sufficiently small. Combining this observation with (2.2.6) we find (2.2.2).

We omit the proof of the next theorem because it follows from theorem 3 in much the same way as theorem 2 follows from theorem 1.

Theorem 4. Let the real function $\psi_n(x)$, vanishing only at isolated points and tending to zero as $|x|$ tends to infinity, be continuous for all $x \in \mathbb{R}$. Assume that $\psi_n(x)$ undergoes exactly n changes of sign for $x \in \mathbb{R}$, and that it satisfies

$$H\psi_n(x) = -\frac{1}{2m}\frac{\mathrm{d}^2}{\mathrm{d}x^2}\psi_n(x) + V(x)\psi_n(x) = E\psi_n(x), \qquad \text{for all } x \in \mathbb{R}, \tag{2.2.11}$$

for some $E \in \mathbb{R}$. $V(x)$ is real and continuous with $(E - V(x)) < 0$ for all sufficiently large $|x|$. Let $\Psi_n(x)$ be any real function, vanishing only at isolated points, which undergoes exactly n changes of sign and is such that $H\Psi_n(x)$ is defined and continuous for all $x \in \mathbb{R}$. Then

$$\mathrm{Inf}\left(\frac{H\Psi_n(x)}{\Psi_n(x)} : x \in \mathbb{R}, \Psi(x) \neq 0\right) \leqslant E. \tag{2.2.12}$$

We remark that the trial function itself need not tend to zero as $|x|$ tends to infinity. The simple choice

$$\Psi(x) = \text{constant} \tag{2.2.13}$$

in theorem 3 yields at once the well known result

$$\min(V(x) : x \in \mathbb{R}) \leqslant E \tag{2.2.14}$$

for any bound state energy E.

Example 3. For the case of the harmonic oscillator potential

$$V(x) = w^2x^2/2m \qquad \text{for some } w \in \mathbb{R}, \tag{2.2.15}$$

we can choose in theorem 3

$$\Psi(x) = \exp(-\gamma x^2), \qquad \gamma \in \mathbb{R}. \tag{2.2.16}$$

This trial function approaches the exact ground state eigenfunction as γ approaches $|w|/2$. We obtain

$$E_0 \geqslant \operatorname*{Inf}_{x \in \mathbb{R}} \left(\frac{2\gamma + (w^2 - 4\gamma^2)x^2}{2m}\right) = \begin{cases} -\infty & \text{if } |\gamma| > |w|/2, \\ \gamma/m & \text{if } 0 \leqslant \gamma \leqslant |w|/2 \end{cases} \tag{2.2.17}$$

and note that as γ approaches $|w|/2$ from below the bound approaches the exact value, while when γ approaches $|w|/2$ from above the bound simply remains equal to minus infinity.

Example 4. Consider the case of the artificial potential

$$V(x) = w^4 x^6/2m, \qquad \text{for some } w \in \mathbb{R}, \tag{2.2.18}$$

chosen because we do not have closed form expressions for the corresponding eigenfunctions and eigenvalues. In theorem 3 we set

$$\Psi(x) = \exp[-w^2 x^4/4\sqrt{3} - (1/12)^{1/4}|w|x^2], \tag{2.2.19}$$

providing the lower bound

$$(1/12)^{1/4}|w|/m \leq E_0. \tag{2.2.20}$$

This compares favourably with the upper bound

$$E_0 \leq (5/36)^{1/4}|w|/m \tag{2.2.21}$$

which follows from the Rayleigh–Ritz principle with trial function

$$\Psi(x) = \exp[-(45/64)^{1/4}|w|x^2]. \tag{2.2.22}$$

To find a lower bound for the first excited state energy we assume that the corresponding eigenfunction has only one node. Then we can have

$$\Psi_1(x) = x \exp[-w^2 x^4/4\sqrt{3} - (25/108)^{1/4}|w|x^2] \tag{2.2.23}$$

in theorem 4, and this yields the lower bound

$$(3/4)^{1/4}|w|/m \leq E_1. \tag{2.2.24}$$

The latter lower bound lies comfortably above the upper bound in (2.2.21).

3. Many-dimensional problems

3.1. The generalisations of theorems 1 and 3

First we consider a quantum mechanical system with N degrees of freedom which is confined to a bounded open domain $D \subset \mathbb{R}^N$ by a real potential $V(x)$ such that

$$V(x) \text{ is } \begin{cases} \text{continuous for } x = (x_1, x_2, \ldots, x_N) \subset \bar{D}, \\ \text{positive infinite for } x \notin \bar{D}. \end{cases} \tag{3.1.1}$$

$\bar{D}$ denotes the closure of D. The boundary ∂D of D is assumed to be sufficiently smooth for the Green theorem to apply, see Miranda (1970). For generality we take Schrödinger's equation for the system to be

$$H\psi(x) = -\sum_{i,j=1}^{N} \frac{\partial}{\partial x_i}\left(p_{ij}(x)\frac{\partial}{\partial x_j}\psi(x)\right) + V(x)\psi(x) = E\psi(x), \qquad x \in D$$

$$\text{with } \psi(x) = 0 \text{ for all } x \in \partial D. \tag{3.1.2}$$

The real functions $p_{ij}(x)$ have continuous first derivatives and are such that the matrix $(p_{ij}(x))$ is strictly positive for all $x \in \bar{D}$.

For such problems it is known that the eigenfunction $\psi_0(x)$ corresponding to the lowest eigenvalue E_0 can be chosen so that $\psi_0(x) > 0$ for all $x \in D$; see Keller and Cohen (1967) for example. This allows us to extend theorem 1.

Theorem 5. For $x \in \bar{D}$ let $\Psi(x)$ be any function not identically zero, such that $H\Psi(x)$ is defined and continuous, and such that $\Psi(x) \geqslant 0$. Then

$$\operatorname{Inf}\left(\frac{H\Psi(x)}{\Psi(x)}: x \in \bar{D}, \Psi(x) \neq 0\right) \leqslant E_0, \tag{3.1.3}$$

where E_0 is the lowest eigenvalue associated with (3.1.2).

Proof. This follows the same lines as the proof of theorem 1. The key point to be established is that one cannot have

$$H\Psi(x) - E_0\Psi(x) \geqslant 0 \qquad \text{for all } x \in D, \tag{3.1.4}$$

with strict inequality somewhere. But if (3.1.4) is true then we must have

$$0 < \int_D \psi_0(x)(H - E_0)\Psi(x)\,\mathrm{d}x = \int_{\partial D} \sum_{i,j=1}^{N} n_i(x) p_{ij}(x)\left(\frac{\partial \psi_0(x)}{\partial x_j}\right)\Psi(x)\,\mathrm{d}x, \tag{3.1.5}$$

where we have used the Green theorem and where $(n_1(x), n_2(x), \ldots, n_n(x))$ denotes the outward unit normal to ∂D. The latter is not possible because $\psi_0(x) = 0$ for all $x \in \partial D$ implies

$$(\partial\psi_0(x)/\partial x_1, \partial\psi_0(x)/\partial x_2, \ldots, \partial\psi_0(x)/\partial x_N) = \alpha(x)(n_1(x), n_2(x), \ldots, n_N(x)), \qquad \text{for all } x \in \partial D, \tag{3.1.6}$$

for some real-valued function $\alpha(x)$, and the positivity of $\psi(x)$ for $x \in D$ implies $\alpha(x) \leqslant 0$ for $x \in \partial D$, so that the right-hand side of (3.1.5) becomes

$$\int_{\partial D} \alpha(x)\left(\sum_{i,j=1}^{N} n_i(x) p_{ij}(x) n_j(x)\right)\mathrm{d}x \leqslant 0. \tag{3.1.7}$$

However, there is no obvious way of extending theorem 2 to more than one dimension. For example, one might suppose that by relaxing the positivity constraint on $\Psi(x)$ in theorem 5 and requiring instead that the nodal surfaces defined by $\Psi(x)$ divide $\bar{D}$ into at most two parts, one will then obtain from the left-hand side of (3.1.3) a lower bound to the first excited state energy of the system. But neither the latter supposition nor anything like it can generally be the case because in more than one dimension there can exist eigenfunctions which correspond to arbitrarily high excitation number and yet whose nodal surfaces divide the fundamental domain into only two parts; see Courant and Hilbert (1953). We find similarly that theorem 4 cannot be generalised.

We extend theorem 3 to the following theorem.

Theorem 6. Let the real function $\psi(x)$, not identically zero but tending to zero as $|x|$ tends to infinity, be continuous for all $x \in \mathbb{R}$ and satisfy

$$H\psi(x) = -\sum_{i,j=1}^{N} \frac{\mathrm{d}}{\mathrm{d}x_i}\left(p_{ij}(x)\frac{\mathrm{d}}{\mathrm{d}x_j}\psi(x)\right) + V(x)\psi(x) = E\psi(x), \qquad \text{for all } x \in \mathbb{R}^N, \tag{3.1.8}$$

for some $E \in \mathbb{R}$. It is assumed that for all x belonging to any closed bounded subset of $\mathbb{R}^N$ the real functions $p_{ij}(x)$ have continuous first derivatives and are such that the matrix $(p_{ij}(x))$ is strictly positive. Furthermore $V(x)$ is real and continuous with $(E - V(x)) < 0$ for all sufficiently large $|x|$. Let $\Psi(x)$ be any real function, vanishing

only on a set of measure zero in $\mathbb{R}^N$, which undergoes no changes of sign and is such that $H\Psi(x)$ is defined and continuous for all $x \in \mathbb{R}$. Then

$$\operatorname{Inf}\left(\frac{H\Psi(x)}{\Psi(x)}: x \in \mathbb{R}^N, \Psi(x) \neq 0\right) \leqslant E. \tag{3.1.9}$$

Proof. We choose $c \in \mathbb{R}^N$ such that $\psi(c) = 1$, and let $D \subset \mathbb{R}^N$ be the largest open connected set containing c such that $\psi(x) \neq 0$ for all $x \in D$. Then for given $0 < \epsilon < 1$ we define $D(\epsilon)$ to be the largest open connected subset of D with $\psi(x) = \epsilon$ for all $x \in \partial D(\epsilon)$. The proof now follows the same lines as the proof of theorem 3 with D and $D(\epsilon)$ replacing (a, b) and $(a(\epsilon), b(\epsilon))$ respectively.

3.2. Simple atomic and molecular systems

We now consider the case where H is the Schrödinger wave operator for an atomic or molecular system, so that in atomic units

$$H = -\sum_{\nu=1}^{M} \frac{1}{2m_\nu}\nabla_\nu^2 - \sum_{i=1}^{N} \frac{1}{2}\nabla_i^2 + \sum_{\mu<\nu} \frac{z_\mu z_\nu}{|\boldsymbol{\Gamma}_\mu - \boldsymbol{\Gamma}_\nu|} - \sum_{\nu=1}^{M}\sum_{i=1}^{N} \frac{z_\mu}{|\boldsymbol{\Gamma}_i - \boldsymbol{\Gamma}_\mu|} + \sum_{i<j} \frac{1}{|\boldsymbol{\Gamma}_i - \boldsymbol{\Gamma}_j|}. \tag{3.2.1}$$

Here m_ν is the mass of the νth nucleus which has charge z_ν; $\boldsymbol{\Gamma}_\nu$ denotes its position vector; and ∇_ν^2 denotes the corresponding Laplacian; $\nu = 1, 2, \ldots, M$. Similarly $\boldsymbol{\Gamma}_i$ and ∇_i^2 refer to the ith electron for $i = 1, 2, \ldots, N$. The system is supposed to admit bound states so that there exists a lowest negative eigenvalue E_0 corresponding to a normalisable eigenfunction $\psi_0(\boldsymbol{\Gamma})$, where

$$\boldsymbol{\Gamma} = (\boldsymbol{\Gamma}_{\nu=1}, \boldsymbol{\Gamma}_{\nu=2}, \ldots, \boldsymbol{\Gamma}_{\nu=M}, \boldsymbol{\Gamma}_{i=1}, \boldsymbol{\Gamma}_{i=2}, \ldots, \boldsymbol{\Gamma}_{i=N}). \tag{3.2.2}$$

Thus

$$H\psi_0(\boldsymbol{\Gamma}) = E_0\psi_0(\boldsymbol{\Gamma}), \qquad \psi_0(\boldsymbol{\Gamma}) \in L_2(\mathbb{R}^{\mathcal{N}}), \tag{3.2.3}$$

where $\mathcal{N} = 3(M+N)$ and $L_2(\mathbb{R}^{\mathcal{N}})$ denotes the Hilbert space consisting of all complex-valued functions which are square-integrable over $\mathbb{R}^{\mathcal{N}}$. We will use the notation

$$\langle f, g\rangle = \int_{\mathbb{R}^{\mathcal{N}}} \bar{f}(\boldsymbol{\Gamma}) g(\boldsymbol{\Gamma})\, d\boldsymbol{\Gamma}, \qquad f, g \in L_2(\mathbb{R}^{\mathcal{N}}) \tag{3.2.4}$$

for the inner product in $L_2(\mathbb{R}^{\mathcal{N}})$.

When we treat H as an operator in $L_2(\mathbb{R}^{\mathcal{N}})$ we shall assume that it is essentially self-adjoint and will then use the same notation H to mean its closure. In this case we will denote its domain by $D(H)$.

In (3.2.3) no antisymmetry requirements are imposed and so $\psi_0(\boldsymbol{\Gamma})$ will be invariant to the interchange of any pair of electron coordinates. Thus for all one- and two-electron systems E_0 will be the physical ground state energy: for ground state two-electron systems the antisymmetry of the total wavefunction comes from the antisymmetry of the spin component $\alpha(1)\beta(2) - \alpha(1)\beta(2)$. More generally we expect that E_0 is itself an extreme underestimate to the true ground state energy because the spatial part of the physically allowed wavefunction is generally much more constrained than $\psi_0(\boldsymbol{\Gamma})$.

Theorem 7. Assume that, in (3.2.3), $\psi_0(\boldsymbol{\Gamma}) \in D(H)$ can be chosen so that it is strictly positive for almost all $\boldsymbol{\Gamma} \in \mathbb{R}^{\mathcal{N}}$. Let $\Psi(\boldsymbol{\Gamma})$ be any function belonging to $D(H)$ which is

strictly positive for almost all $\Gamma \in \mathbb{R}^{\mathcal{N}}$. Then

$$\mathrm{Inf}\left(\frac{H\Psi(\Gamma)}{\Psi(\Gamma)}: \Gamma \in \mathbb{R}^{\mathcal{N}}, \Psi(\Gamma) \neq 0\right) \leqslant E_0. \tag{3.2.5}$$

Proof. Let Ω be any subset of $\mathbb{R}^{\mathcal{N}}$ with non-zero measure. Then we show that it is impossible to have

$$H\Psi(\Gamma) - E_0\Psi(\Gamma) \begin{cases} \geqslant 0 & \text{for almost all } \Gamma \in \mathbb{R}^{\mathcal{N}} \\ > 0 & \text{for almost all } \Gamma \in \Omega. \end{cases} \tag{3.2.6}$$

For suppose (3.2.6) is true. Then it follows that

$$\langle \psi_0, (H - E_0)\Psi \rangle > 0. \tag{3.2.7}$$

But because H is self-adjoint and both ψ_0 and Ψ belong to $D(H)$ we have

$$\langle \psi_0, (H - E_0)\Psi \rangle = \langle (H - E_0)\psi_0, \Psi \rangle = 0, \tag{3.2.8}$$

which contradicts (3.2.7).

Hence (3.2.6) is false, and there must exist a subset σ of $\mathbb{R}^{\mathcal{N}}$ of non-zero measure such that

$$H\Psi(\Gamma) - E_0\Psi(\Gamma) \leqslant 0 \qquad \text{for almost all } \Gamma \in \sigma. \tag{3.2.9}$$

(3.2.5) is now implied because we also have

$$\Psi(\Gamma) > 0 \qquad \text{for almost all } \Gamma \in \sigma. \tag{3.2.10}$$

An alternative approach to lower bounds on E_0 is possible. Instead of working in a Hilbert space framework one extends theorem 6 with the aid of an assumption. Such an approach is of interest because it maintains a consistency with the ideas introduced earlier in the paper: the result is that more flexible trial functions, no longer required to belong to $D(H)$, can be utilised to obtain lower bounds for E_0.

We cannot directly apply the kind of argument used in § 3.1 to the present systems because of the singularities occurring in the Coulombic potentials. This difficulty is side-stepped by introducing an assumption as follows. Let $1 > \delta > 0$ be given and correspondingly define

$$V^{\delta}_{\mu,\nu}(\Gamma) = \begin{cases} 1/\delta & \text{when } 0 \leqslant |\Gamma_\mu - \Gamma_\nu| < \delta, \\ z_\mu z_\nu / |\Gamma_\mu - \Gamma_\nu| & \text{when } \delta \leqslant |\Gamma_\mu - \Gamma_\nu| \leqslant 1/\delta, \\ 0 & \text{when } 1/\delta < |\Gamma_\mu - \Gamma_\nu|. \end{cases} \tag{3.2.11}$$

Analogously, define approximate Coulombic potentials $V^{\delta}_{i,\nu}(\Gamma)$ and $V^{\delta}_{i,j}(\Gamma)$ associated with the electron–nucleus and electron–electron interactions respectively, so that the potential energy term in (3.2.1) is approximated by the continuous function

$$V^{\delta}(\Gamma) = \sum_{\mu<\nu} V^{\delta}_{\mu,\nu}(\Gamma) + \sum_{\nu=1}^{M} \sum_{i=1}^{N} V^{\delta}_{i,\nu}(\Gamma) + \sum_{i<j} V^{\delta}_{ij}(\Gamma), \tag{3.2.12}$$

and H is approximated by

$$H^{\delta} = -\sum_{\nu=1}^{M} \frac{1}{2m_\nu} \nabla_\nu^2 - \sum_{i=1}^{N} \tfrac{1}{2} \nabla_i^2 + V^{\delta}(\Gamma). \tag{3.2.13}$$

Assumption. For all sufficiently small $\delta > 0$ there exists a least real number E_0^δ, belonging to a continuous real function $\psi_0^\delta(\mathbf{\Gamma})$, such that

$$H^\delta \psi_0^\delta(\mathbf{\Gamma}) = E_0^\delta \psi_0^\delta(\mathbf{\Gamma}) \qquad \text{for all } \mathbf{\Gamma} \in \mathbb{R}^{\mathcal{N}} \tag{3.2.14}$$

where

$$\text{either} \quad E_0^\delta < E_0, \quad \text{or else} \quad \lim_{\delta \to 0} E_0^\delta = E_0. \tag{3.2.15}$$

The function $\psi_0^\delta(\mathbf{\Gamma})$ is required to be not identically zero, and to tend to zero as $|\mathbf{\Gamma}|$ tends to infinity.

This assumption is roughly of the kind made in quantum mechanical perturbation theory, and seems likely to be true because the approximate potential approaches the true Coulombic potential as δ tends to zero while having the same symmetries.

Provided that the above assumption is true we can apply theorem 6 to obtain lower bounds for E_0. Namely, for any real function $\Psi(\mathbf{\Gamma})$, vanishing only on a set of measure zero in $\mathbb{R}^{\mathcal{N}}$, which undergoes no changes of sign and is such that $H^\delta \Psi(\mathbf{\Gamma})$ is defined and continuous for all $\mathbf{\Gamma} \in \mathbb{R}^{\mathcal{N}}$, we must have

$$\operatorname{Inf}\left(\frac{H^\delta \Psi(\mathbf{\Gamma})}{H(\mathbf{\Gamma})} : \mathbf{\Gamma} \in \mathbb{R}^{\mathcal{N}}, \Psi(\mathbf{\Gamma}) \neq 0 \right) \leqslant E_0^\delta \tag{3.2.16}$$

for all sufficiently small δ. Hence, if the limit exists, we obtain using our assumption (3.2.15)

$$\lim_{\delta \to 0} \operatorname{Inf}\left(\frac{H^\delta \Psi(\mathbf{\Gamma})}{\Psi(\mathbf{\Gamma})} : \mathbf{\Gamma} \in \mathbb{R}^{\mathcal{N}}, \Psi(\mathbf{\Gamma}) \neq 0 \right) \leqslant E_0. \tag{3.2.17}$$

Example 5. For a hydrogen-like system with nuclear charge z we have

$$H = -\tfrac{1}{2}\nabla^2 - z/|\mathbf{\Gamma}|, \qquad \mathbf{\Gamma} \in \mathbb{R}^3. \tag{3.2.18}$$

We can apply theorem 7 with the choice of trial function

$$\Psi(\mathbf{\Gamma}) = \mathrm{e}^{-\alpha|\mathbf{\Gamma}|}, \qquad \alpha > 0, \tag{3.2.19}$$

which becomes the exact ground state eigenfunction when $\alpha = z$. Then (3.2.5) gives

$$E_0 \geqslant \operatorname*{Inf}_{\mathbf{\Gamma} \in \mathbb{R}^3} [-\tfrac{1}{2}\alpha^2 + (\alpha - z)/|\mathbf{\Gamma}|] = \begin{cases} -\infty & \text{if } \alpha < z, \\ -\tfrac{1}{2}\alpha^2 & \text{if } \alpha \geqslant z. \end{cases} \tag{3.2.20}$$

In particular, the lower bound smoothly approaches the exact value ($E_0 = -\frac{1}{2}z^2$) as α approaches z through values greater than z. Notice that $H\Psi/\Psi$ possesses a polar singularity except when $\alpha = z$.

Alternatively, provided with our assumption *circa* (3.2.14), we can use the trial function

$$\Psi(\mathbf{\Gamma}) = 1/(1 + z|\mathbf{\Gamma}|) \tag{3.2.21}$$

which does not belong to $D(H)$. Then (3.2.17) yields the crude bound

$$E_0 \geqslant -2z^2. \tag{3.2.22}$$

Example 6. For a helium-like system with nuclear charge z we have

$$H = -\tfrac{1}{2}\nabla_1^2 - \tfrac{1}{2}\nabla_2^2 - z/|\mathbf{\Gamma}_1| - z/|\mathbf{\Gamma}_2| + 1/|\mathbf{\Gamma}_1 - \mathbf{\Gamma}_2|. \tag{3.2.23}$$

The simple choice of trial function

$$\Psi(\boldsymbol{\Gamma}_1, \boldsymbol{\Gamma}_2) = e^{-\alpha(|\boldsymbol{\Gamma}_1|+|\boldsymbol{\Gamma}_2|)}, \qquad \alpha > 0 \tag{3.2.24}$$

in theorem 7 gives the bounds

$$E_0 \geqslant \inf_{\boldsymbol{\Gamma}_1 \in \mathbb{R}^3, \boldsymbol{\Gamma}_2 \in \mathbb{R}^3} [-\alpha^2 + (\alpha - z)(1/|\boldsymbol{\Gamma}_1| + 1/|\boldsymbol{\Gamma}_2|) + 1/|\boldsymbol{\Gamma}_1 - \boldsymbol{\Gamma}_2|] = \begin{cases} -\infty & \text{if } \alpha < z \\ -\alpha^2 & \text{if } \alpha \geqslant z. \end{cases} \tag{3.2.25}$$

We have tried to improve this result by using more elaborate trial functions, but without success. However, Bartlett (1955) has obtained an approximate wavefunction for the ground state of helium in numerical form. This wavefunction was obtained by an iterative procedure which was designed to make the fluctuations in the local energy as small as possible! Over all the calculated points, corresponding to values of $|\boldsymbol{\Gamma}_1|$ and $|\boldsymbol{\Gamma}_2|$ up to about 4 au, the local energy lay between $-2{\cdot}92$ au and $-2{\cdot}88$ au. The foregoing theory suggests, but does not on its own prove, that $-2{\cdot}92$ au is a lower bound for the ground state energy of helium.

Example 7. For systems such as H_2^+, when the Born–Oppenheimer approximation is made, one obtains

$$H = -\tfrac{1}{2}\nabla^2 - z/|\boldsymbol{\Gamma}| - z/|\boldsymbol{\Gamma} + \boldsymbol{R}| + z^2/|\boldsymbol{R}|, \qquad \boldsymbol{\Gamma} \in \mathbb{R}^3 \tag{3.2.26}$$

where the origin of coordinates is at one of the two nuclei, $\boldsymbol{R}$ is the fixed position vector for the other nucleus, and each nucleus has charge z. Applying theorem 7 with trial function

$$\Psi(\boldsymbol{\Gamma}) = e^{-\alpha|\boldsymbol{\Gamma}| - \alpha|\boldsymbol{\Gamma}+\boldsymbol{R}|}, \qquad \alpha > 0, \tag{3.2.27}$$

we discover

$$\frac{H\Psi(\boldsymbol{\Gamma})}{\Psi(\boldsymbol{\Gamma})} = -\alpha^2\left(1 + \frac{\boldsymbol{\Gamma}.(\boldsymbol{\Gamma}+\boldsymbol{R})}{|\boldsymbol{\Gamma}||\boldsymbol{\Gamma}+\boldsymbol{R}|}\right) + (\alpha - z)\left(\frac{1}{|\boldsymbol{\Gamma}|} + \frac{1}{|\boldsymbol{\Gamma}+\boldsymbol{R}|}\right) + \frac{z^2}{|\boldsymbol{R}|}. \tag{3.2.28}$$

Hence for the ground state energy $E_0(|\boldsymbol{R}|)$ we have on putting $\alpha = z$ the lower bound

$$E_0(|\boldsymbol{R}|) \geqslant -2z^2 + z^2/|\boldsymbol{R}|, \tag{3.2.29}$$

which behaves correctly as $|\boldsymbol{R}|$ tends to zero. To obtain a bound which tends to the correct limit as $|\boldsymbol{R}|$ tends to infinity we use the trial function

$$\Psi(\boldsymbol{\Gamma}) = e^{-\alpha|\boldsymbol{\Gamma}|} + e^{-\alpha|\boldsymbol{\Gamma}+\boldsymbol{R}|}, \qquad \alpha > 0. \tag{3.2.30}$$

Then if α is chosen to satisfy

$$\alpha = z(1 + e^{-\alpha|\boldsymbol{R}|}), \tag{3.2.31}$$

we find after some analysis that

$$E_0(|\boldsymbol{R}|) \geqslant -\tfrac{1}{2}\alpha^2 - 2z(1 - e^{-\alpha|\boldsymbol{R}|})/|\boldsymbol{R}| + z^2/|\boldsymbol{R}| = E_0^{\mathrm{L}}(|\boldsymbol{R}|). \tag{3.2.32}$$

The lower bound $E_0^{\mathrm{L}}(|\boldsymbol{R}|)$ is worse than the lower bound (3.2.29) when $|\boldsymbol{R}|z < 1{\cdot}242$, and better than it when $|\boldsymbol{R}|z > 1{\cdot}243$. For $|\boldsymbol{R}|z > 5$ we find that to a good approximation

$$E_0^{\mathrm{L}}(|\boldsymbol{R}|) \sim -\tfrac{1}{2}z^2 + (z^2 - 2z)/|\boldsymbol{R}|, \tag{3.2.33}$$

so that $E_0^{\mathrm{L}}(|\boldsymbol{R}|) \to E_0(|\boldsymbol{R}|)$ as $|\boldsymbol{R}| \to \infty$. We note that the Rayleigh–Ritz upper bound

$E_0^U(|\boldsymbol{R}|)$ which is obtained using the trial function (3.2.31) wherein $\alpha = z$, behaves for large $|\boldsymbol{R}|$ according to

$$E_0^U(|\boldsymbol{R}|) \sim -\tfrac{1}{2}z^2 + (z^2 - z)/|\boldsymbol{R}|. \tag{3.2.34}$$

Although the lower bounds obtained in this problem are of a simple form, they are crude by the standards usually applied to such problems. For example, at $|\boldsymbol{R}| = 5$ with $z = 1$ our lower bound is $-0{\cdot}7$ whilst the exact energy is $-0{\cdot}5244$. Furthermore it would require considerable effort to improve the bounds.

Acknowledgments

The author thanks Professor G Fichera for supplying some of the references and Dr P Moussa for giving encouragement. He also thanks a referee for helpful criticisms of the original manuscript.

References

Barta J 1937 *C.R. Acad. Sci., Paris* **204** 472
Bartlett J H 1955 *Phys. Rev.* **98** 1067
Bethe H A and Salpeter E E 1957 *Quantum Mechanics of One- and Two-Electron Atoms* (Berlin: Springer)
Birkhoff G and Rota G 1962 *Ordinary Differential Equations* (Boston: Ginn)
Boggio T 1907 *Atti Acad. Naz. Lincei* **26** 386
Breuer S and Gottlieb D 1971 *J. Math. Anal. Applic.* **36** 465
Courant R and Hilbert D 1953 *Methods of Mathematical Physics* vol. 1 (New York: Interscience)
Duffin R J 1947 *Phys. Rev.* **71** 827
Fichera G 1954 *Annali Mat. Pura Appl.* **36** 273
Frost A A 1942 *J. Chem. Phys.* **10** 240
Hersch J 1959 *C.R. Acad. Sci., Paris* **249** 1074
Keller H B and Cohen D S 1967 *J. Math. & Mech.* **16** 1361
Miranda C 1970 *Partial Differential Equations of Elliptic Type* (Berlin: Springer) 2nd revised edn (translated by Z C Motteler)
Picard E 1893 *Traité d'Analyse*, vol. 2, 1st edn (Paris: Gauthier-Villars) pp 25–6
Protter M H and Weinberger H F 1967 *Maximum Principles in Differential Equations* (Englewood Cliffs, NJ: Prentice-Hall)
Redheffer R 1966 *J. Math. Anal. Applic.* **16** 219
Stanton R E and Taylor R L 1966 *J. Chem. Phys.* **45** 565