A Family of Optimal Conditions for the Absence of Bound States in a Potential

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A FAMILY OF OPTIMAL CONDITIONS FOR THE ABSENCE OF BOUND STATES IN A POTENTIAL

V. Glaser and A. Martin
CERN -- Geneva

and

H. Crosse and W. Thirring
Institut für Theoretische Physik
der Universität Wien

ABSTRACT

We derive the optimal condition

$$I_p(V) = \frac{(p-1)^{p-1} \Gamma(2p)}{p^{p-2} \Gamma(p)} \int \frac{d^3x}{4\pi} |x|^{2p-3} |\psi^n(x)|^2 \left| V^n(x) \right|^p < 1$$

for the absence of bound states in a potential. The condition is valid

i) for arbitrary $V$ if $p > \frac{3}{2}$;

ii) for spherically symmetric $V$ if $1 \leq p \leq \frac{3}{2}$.

In the special case of spherical symmetry, the number of bound states with angular momentum $l$ is less than $(2l+1)^{1-2p} I_p(V)$. An application for mesic atoms is presented.
1. INTRODUCTION

A standard problem in Schrödinger's theory is to obtain conditions on a potential in order to guarantee that this potential has at most one or n bound states. For instance, Jost and Pais\textsuperscript{1)}, Bargmann\textsuperscript{2)}, and Schwinger\textsuperscript{3)} have shown that a spherically symmetric potential such that

\[ \int V(r) r \, dr < 1 \]  
\[ \text{(1)} \]

where \( V^- > 0 \) is the attractive part of the potential, with units such that \( 2m/h^2 = 1 \), has no bound states. Similarly, it is also known\textsuperscript{4)} that if

\[ \sup r = V(r) < 1/4 \]  
\[ \text{(2)} \]

there is no bound state. Bargmann has also obtained that in the state of angular momentum \( \ell \) the number of bound states \( v_\ell \) (counted without the \( 2\ell + 1 \) multiplicity factor) is such that

\[ (2\ell + 1) v_\ell < \int r V(r) \, dr \]
\[ \text{(3)} \]

On the other hand, Faris\textsuperscript{5)} has obtained an inequality of the type

\[ \int d^3x \left| V^- (x) \right|^{3/2} < C \]  
\[ \text{(4)} \]

for arbitrary potentials, not necessarily spherically symmetric, and one of us\textsuperscript{6)}, in the special limit of a fixed shape potential, has obtained the asymptotic estimate, for \( V = \lambda v \), \( \lambda \to \infty \)

\[ N \sim \frac{1}{6\pi^2} \int d^3x \left| V^- (x) \right|^{3/2}. \]
\[ \text{(5)} \]

What we want to do here is to find a complete family of optimal inequalities, incorporating inequalities (1) and (2) as extreme cases. Formulae (1) and (2) are already optimal, in the sense that the numerical constants they contain cannot be improved. Inequality (4), on the other hand, is not yet optimal. The inequalities we shall obtain in Section 2 involve arbitrary powers of the potential \( \left[ V^- (r) \right]^p \), \( 1 \leq p \leq \infty \) and are all optimal, as shown in Section 3. Comparison with standard potentials shows that for a convenient \( p \) they give excellent results. In Section 4 an application to muonic atoms is given, which gives relatively tight bounds on the ground-state energy levels.

For monotonic potentials, other conditions can be derived. In particular, Calogero\textsuperscript{7)} has obtained

\[ \int V(r) \, dr < \frac{\pi}{2} \]  
\[ \text{(6)} \]
Conditions involving powers of $V < 1$ will be investigated in a forthcoming publication by one of us (H.G.).

2. PRESENTATION OF THE NEW INEQUALITIES

The ground state of the Schrödinger equation

$$-\Delta \psi + V(x) \psi(x) = E \psi(x)$$

(7)

if it exists, must have a negative energy $E_0$ given by the variational principle

$$E_0 = \inf_{\|\psi\|_2 = 1} H(\psi)$$

(8)

$$H(\psi) = \int (\psi^2) d^3x + \int V(x)(\psi(x))^2 d^3x$$

$$= \|\nabla \psi\|^2_2 + (\psi, \psi)$$

Here it is assumed that the potential $V$ is a (not necessarily centrally symmetric) real function which vanishes sufficiently rapidly at infinity. In (8) the infimum is taken over the Hilbert space $\mathcal{H}_V$ of functions for which $\psi, \psi$, and $|\psi|^2$ are square integrable, but it may also be taken over any space of smoother functions which is dense in $\mathcal{H}_V$, e.g. the space $\mathcal{H}$ of infinitely differentiable functions with compact support. Also there is no loss of generality if we assume these functions to be real-valued.

Let $V = V_+ - V_-, V_+ \geq 0$, be the decomposition of $V$ into its positive and negative parts, and let $r = |x - y|$, where $y$ is an arbitrarily chosen fixed point in $\mathbb{R}_3$. Then we have for an arbitrary real $\alpha$ the Hölder inequality

$$\int V_- \psi^2 d^3x \leq \left\{ \int (r^\alpha V_-) \psi^2 d^3x \right\}^{1/\alpha} \left\{ \int (r^{\alpha + 1 - \alpha} \psi^2) d^3x \right\}^{\alpha/(\alpha + 1)}$$

(9)

$$= \|r^\alpha \psi\|_p \|r^{\alpha + 1 - \alpha} \psi\|_{1/\alpha}$$

for any $1 \leq p \leq \alpha$, $\frac{1}{\alpha} + \frac{1}{1/\alpha} = 1$

We thus obtain a lower bound for the functional $H$

$$H(\psi) \geq \|\nabla \psi\|_2^2 - \|r^\alpha \psi\|_p \|r^{\alpha + 1 - \alpha} \psi\|_{1/\alpha}^2$$

(10)

(Note that for some $\alpha$ and $p$ the right-hand side of (9) can be $\infty$.) We shall now choose $\alpha$ so that the quantity $\|r^\alpha \psi\|_p \equiv N_p (V_-, y)$ is dimensionless. Since $V$ has dimension (length)$^{-2}$ we get the relation

$$p(2 - \alpha) = 3$$

(11)

$$q(1 + \alpha) = 3$$

Under this condition the norm $\|r^{-\alpha/2} \psi\|_{2q}$ has the same dimension as $\|\psi\|_2$, which means that the functional

$$F_q (\psi) = \frac{\|\nabla \psi\|_2^2}{\|r^{(1-3\alpha)/2} \psi\|_{2q}^2} = \frac{\int (\nabla \psi)^2 d^3x}{\left[ \int r^{(1-3\alpha)/2} \psi^2 d^3x \right]^{1/2}}$$

(12)
remains unchanged under the scale transformations ψ(χ) → λψ(ρχ) (λ, ρ ≠ 0). In (12) we have assumed r = |x| without loss of generality. If we denote

$$μ_q = \inf_{0 ≠ ψ < R} F_q(ψ) ≥ 0$$

then (10) can be written

$$H(ψ) ≥ \{ μ_q - N_p(ψ, y) \} \| r^{(q-3)/2q} ψ \|_2^2$$

where

$$N_p(ψ, y) = \int |y - x|^{2p-3} ψ(x)^2 dx.$$  \hspace{1cm} (15)

The inequality (14) is the starting point of our paper. For suppose a) that for some 1 < q < ∞, μ_q is strictly positive, and b) that for some y ∈ R³ we have the inequality

$$μ_q - N_p(ψ, y) > 0.$$  \hspace{1cm} (16)

Then it follows from (14) that the potential V cannot give rise to a bound state. In the case μ_q > 0, (14) can be written in the equivalent form

$$H(ψ) ≥ \| r^{(q-3)/2q} ψ \|_2^2 \{ 1 - N_p(ψ, y) \}. \hspace{1cm} (14')$$

Our aim is to determine the numbers μ_q. Since the functional F_q is invariant under rotations around the origin, we might make the naive supposition that the infimum of F_q is to be sought among centrally symmetric functions ψ = ψ(r). It turns out that the minimization of the functional

$$F_q^R = \text{restriction of } F_q \text{ to centrally-symmetric } ψ$$

is a relatively simple task: the numbers μ_q can be explicitly computed and turn out to be strictly positive for 1 ≤ q ≤ ∞ (see Theorem 1 below).

This naive argument is, however, wrong in the case q > 3, i.e. 1 ≤ p < 3/2: although μ_q^R = inf F_q^R > 0 we have

$$μ_q = 0 \text{ for } q > 3, \text{ i.e. } 2p - 3 < 0. \hspace{1cm} (18)$$

For suppose μ_q were positive, take a potential V = -V of compact support deep enough so that it can bind a particle (a spherical square-well will do). Then because of 2p-3 < 0 the integral (15) can be made as small as we like by taking |y| big enough, in particular so small that inequality (16) is fulfilled. This contradicts the fact that there is a negative bound state and hence (18) follows.
The above argument does not work for $2p-3 > 0$. In fact we have the

**Proposition 1:** For $1 < q < 3$, i.e. $p > \frac{3}{2}$,

\[
\ln F_q^* = \ln F_q^R
\]  

For the proof we first remark that we can restrict ourselves to non-negative $\psi$'s, because replacing $\psi$ by $|\psi|$ will not change $F_q^* \left[ \nabla |\psi| = c(\psi) \nabla \psi \right]$. Then we use the following theorem:

**Theorem 1:** Given $\psi(x) \geq 0$, define $\psi_R(|x|)$, the spherical decreasing rearrangement of $\psi$: $\psi_R$ is a decreasing function of $|x| = r$ such that for every non-negative constant $M$ the Lebesgue measure $\mu[\psi_R(|x|) \geq M] = \mu[\psi(|x|) \geq M]$. Then

\[
a) \quad \int \nabla \psi \, d^3x \geq \int \nabla \psi_R \, d^3x \quad \text{and} \\
b) \quad \int \chi \, \psi \, d^3x \leq \int \chi_R \, \psi_R \, d^3x
\]

where $\chi$ and $\psi$ are any two positive functions.

Part (b) of this theorem has been known for a long time, while part (a) is presumably new, so that its proof is given in Appendix A.

We take $\chi = r^{q-3}$. For $q \leq 3$, $\chi$ is decreasing and $\chi_R = \chi$. We have also evidently $(\psi^2)_R = \psi_R^2$, so that $F_q(\psi) \geq F_q(\psi_R)$. This is just our statement (19).

For the spherically symmetric functional we have

**Theorem 2:** For $1 < q < \infty$ the functional $F_q^R$ has the strictly positive infimum

\[
\kappa_q^R = \frac{4}{p-1} \left[ \frac{2^{q-1}}{(q-1) \Gamma(q)} \right]^{1/4}, \quad \frac{1}{p} + \frac{1}{q} = 1
\]  

which is attained by the uniquely determined family of functions

\[
\psi_q = \frac{a}{(1 + b r^{1/(p-1)})^{p-1}}
\]  

where the arbitrary constants $a$ and $b$ reflect the scale invariance of the problem.

We can prove this theorem by using an old result of Bliss. However, we prefer to give a new straightforward proof. Even this proof is a bit delicate and it will be given in Appendix B. Let us give here only the formal calculation leading to (20) and (21).

By the change of variables

\[
\phi = r^n \psi \quad \kappa = ln r
\]
the functional $F^R_q$ takes the form

$$F^R_q = (4\pi)^k G_{2q}(\phi), \quad G_{2q}(\phi) = \frac{\int_0^{\infty} \left[ \left( \frac{d\phi}{dx} \right)^2 + \frac{1}{4} \phi^2 \right] dx}{\int_0^{\infty} \phi^{2q} dx} = \frac{I}{J^{1/2q}}$$

and the naive variation equation $\delta G(\phi) = 0$ gives us the differential equation

$$\phi'' = \frac{3}{4} \phi - \kappa \phi^{k-1}, \quad \kappa = \frac{I}{J}, \quad 2 < k < 2q < \infty$$

which we have to solve under the initial condition

$$\phi(\pm \infty) = \phi'(\pm \infty) = 0$$

since the integrals $I$ and $J$ have to converge. The first integral of (24) is given by

$$\phi' = \frac{1}{4} \phi - \frac{2\kappa}{k} \phi^k$$

The arbitrary additive constant in the right-hand side of (26) was set equal to zero in accordance with (25). By the change of scale $\phi \rightarrow (k\phi/\kappa)^{1/k} \phi$, the equations (26) and (24) take the simpler form

$$\phi' = \frac{1}{4} (\phi - \phi^k), \quad \phi'' = \frac{3}{4} \phi - \frac{k}{\kappa} \phi^{k-1}$$

[Notice that $G_k$ is invariant under the transformations $\phi(x) \rightarrow \lambda \phi(x-a)$.] Up to a translation the solutions of (26') are given by inversion of the integral

$$\int_{\phi}^{\infty} \frac{2dt}{t^{1-t_k/2}} = |x|, \quad 2 < k < \infty$$

The substitution $t^{k-2} = 1 - u^2$ leads to an elementary integral with the result

$$\phi_q(x) = \left[ \cos k (q-1) \frac{x}{\kappa} \right]^{-k/(q-1)}$$

which is precisely formula (21) in the old variables.

It remains to compute the minimal value $\nu_k = G_k(\phi_k)$. For the sake of comparison with the results of Appendix B we shall give the details of this calculation. By multiplying the second equation (26') with $\phi$ and integrating over $(-\infty, +\infty)$ we get $I(\phi_k) = (k/\kappa) J(\phi_k)$ so that $\nu_k = I \cdot \frac{1}{k/2} = (k/\kappa) J^{1-2/k}$. The integral $J$ is computed with the change of variables $dx = 2dt/\sqrt{1-t^{k-2}}$ to

$$J = 4 \int_{-1}^{1} \frac{t^{k-2} dt}{\sqrt{1-t^{k-2}}}$$
This integral can be expressed in terms of $\Gamma$-functions, which leads to formula (20) of Theorem 2.

Note: It is easily verified on the expression (17) that
\[
\lim_{p \to 1} \mu_q^p = 4\pi, \quad \lim_{p \to \infty} \mu_q^p = \frac{4}{\pi}
\]
so that $\mu$ is strictly positive for $1 \leq p \leq \infty$.

The case $p = 1$ corresponds to the Bargmann inequality\(^2\) for the absence of bound states $\int r |V(r)| dr < 1$. The case $p \to \infty$ corresponds to the condition $\sup r^2 |V(r)| < \frac{1}{2}$ which can be found in Courant and Hilbert\(^4\). The only translation-invariant condition is the one obtained for $p = \frac{3}{2}$.

Let us end this section by pointing out another amusing fact which illustrates the necessity of a rigorous proof of Theorem 1. Let $F_q^a$ be the restriction of the functional $F_q^R$ to functions which vanish outside and on the boundary of a sphere of finite radius $a$. Then, as shown in Appendix B, the infimum of $F_q^a$ is the same as that of $F_q^R$ but there is no function which saturates that minimum.

3. DISCUSSION OF INEQUALITY (14)

Proposition 1 and Theorem 2 show that the criterion (16) for the absence of bound states is indeed valid as it stands for all $p \geq \frac{3}{2}$ with $\mu_q$ given by formula (20) for any potential. For spherically-symmetric potentials $V = V(r)$ however, Theorem 2 allows us to exploit the whole range $1 < p < \infty$ in the following way.

For a wave function of angular momentum $\ell$ of the form $\psi(r)P^\ell(\cos \theta)$, the expectation value of the total energy takes the form
\[
H_\ell(\psi) = \int \left\{ \left( \frac{\partial \psi}{\partial r} \right)^2 + \frac{\ell(\ell+1)}{r^2} \psi^2 + V \psi^2 \right\} r^2 dr
\]
If we subject this functional to the same manipulations, we are led to the minimization of the functional
\[
(4\pi)^{\frac{3}{2}} F_\ell^q(\psi) = \int \left\{ \psi^2 + \frac{\ell(\ell+1)}{r^2} \psi^2 \right\} r^2 dr \left[ \int r^{q-3} \psi^2 r^2 dr \right]^{-\frac{q}{2}}
\]
The change of variables (22) then leads to the functional $G_\ell^q$, which differs from the old one (23) only through the replacement $\frac{1}{2} \phi^2 \to \left[ (2\ell + 1)^2 / 4 \right] \phi^2$. By the scale transformation $\phi(x) = \phi, [ (2\ell + 1) x ]$ we get back to the old functional
\[
(4\pi)^{\frac{3}{2}} F_\ell^q(\psi) = G_\ell^q(\phi) = (2\ell+1)^{\frac{1}{2}+\frac{q}{2}} G_\ell^q(\phi_1)
\]
for which we know the infimum. Therefore the criterion for the absence of a bound state in the $\ell$th partial wave reads
Of course, when $p \geq \frac{1}{2}$ and $l = 0$ we may replace $r^{2p-1}$ by $|x-y|^{2p-1}$ in this formula, where $y$ is an arbitrary point in space. The corresponding minimizing functions are given by

$$
\phi_{q,l}(x) = \left[1+\frac{1}{2}\right]^{1/2} \left[1+\frac{\left|x-y\right|}{2}\right]^{1/2} \psi_{q,l} \frac{ar^l}{(1+br^{2l+1})^{1/2}}
$$

We want to show that, given a fixed $p$, the bound we have obtained is the best one in the following sense: the numerical constant $\mu_p$ appearing in the inequalities (16) and (34) cannot be replaced by any smaller number. The reason is the following: let $\psi_{q,l}$ be a function (35) minimizing the functional (34) and $u_{q,l} = r\psi_{q,l}$ the corresponding reduced wave function. Then we define a potential $v_{q,l}$ by the equation

$$
\left\{-\frac{d^2}{dr^2} + \frac{l(l+1)}{r^2}\right\} u_{q,l} + v_{q,l} u_{q,l} = 0
$$

so that $u_{q,l}$ may be regarded as the zero energy solution of the Schrödinger equation (36) with the potential $v_{q,l}$. Now, according to (35) $u_{q,l} \approx a \lambda^{q+1}$ for $r \to 0$ and $\approx \text{const } r^{-\lambda}$ for $r \to \infty$, which are precisely the conditions of a zero energy bound state. From (36) we find

$$
\nu_{q,l} = -\lambda^{-q-3} \psi_{q,l}^{2q-2}
$$

Now if we choose $V = v$ in the Schrödinger equation (7) we find that in the Hölder inequality (9) actually the equality sign holds because the three integrands $v_2 \psi_2$, $(r^2 v_2)^P$, and $(r^{-\alpha} \psi_2)^q$ are all proportional to each other in view of (37). This also implies $u_0 = \text{const } (v_{q,l}) = 0$, which proves our assertion.

Note: From (35) and (37) it follows that "the saturating potentials" have the following behaviour:

$$
-\nu_{q,l} \approx \text{const } r^{q-3+2(q-1)\lambda} \quad , \quad -\nu_{q,l} \approx \text{const } r^{-2(9+1)\lambda} \quad \text{for } r \to 0
$$

Since they depend on several parameters, they are well suited as "comparison potential" for a given potential $V$.

We give a practical illustration of this fact in Table 1, where we give the minimum strength of some classical potentials (square well, exponential, Yukawa,
Gaussian) necessary to produce a bound state. The "exact" result is taken from Blatt and Weisskopf and comes from a numerical solution of the Schrödinger equation. We also give the Bargmann bound, the bound for $\rho = \frac{3}{2}$, and the optimal bound. Except for the square well, the $\rho = \frac{3}{2}$ bound is already excellent (within 2-3% of the exact results). Optimizing with respect to $\rho$ reduces the discrepancy to less than 1% for the smooth potentials and 4% for the square well.

For the case of spherically-symmetric potentials another generalization can be made to the case of more bound states. It is well known that if we have $v_\ell$ bound states with strictly negative energy with angular momentum $\ell$ (not counting the $2\ell + 1$ degeneracy) the zero energy radial reduced wave function has $v_\ell$ zeros, excluding the origin. Then, if $r_\rho$ and $r_{\rho+1}$ are successive nodes, we get

$$0 = \int_{r_\rho}^{r_{\rho+1}} \left( \frac{d\psi}{dr} \right)^2 + \ell^2 \rho^2 \psi^2 + \nu \psi^2 \right) \, dr$$

and we can apply to this finite interval all the chain of inequalities previously derived because they are valid for continuous functions with compact support. In this way, adding up the inequalities we get a bound on the number of bound states:

$$v_\ell (2\ell+1)^{2\ell+1} < \left( \frac{p+1}{p} \right)^{2\ell+1} \frac{1}{\rho^2} \int_0^\infty r^{2\ell+1} \nu^\ell(r) \, dr$$

(39)

It is known that, at least in the case $\rho = 1$, inequality (39) cannot be improved, even for $v_\ell > 1$. We believe that no substantial improvement can be achieved for different values of $\rho$. However, let us point out that if inequality (39) is saturated it will be only for one given value of $\ell$. If, for instance, we try to sum (39) over the various values of $\ell$, we will get an overestimate of the number of bound states. For instance, if we take $\rho = \frac{3}{2}$, we get for the total number of bound states in a spherically-symmetric potential

$$N = \sum_0^{\ell_{\text{max}}} v_\ell (2\ell+1) < I \sum_0^{\ell_{\text{max}}} 1/(2\ell+1)$$

(40)

with $2\ell_{\text{max}} + 1 = \sqrt{I}$

$$I = \frac{16}{3\sqrt{3}} \int_0^\infty r^2 |\nu(r)|^2 \, dr$$

(41)

We have therefore

$$N < I \left[ 1 + \frac{1}{4} \ln I \right] \quad \text{for } I \geq 1 .$$

(42)
This is a strict bound valid for spherically-symmetric potentials. This can be compared with the asymptotic estimate

\[ N \sim \frac{1}{6\pi^2} \int |V^{-2/3}|^2 \, d^3x = \frac{\sqrt{3}}{2} I \]  

(43)

valid for \( V = \lambda \bar{v}^2 \), \( \lambda \to +\infty \), \( \bar{v} \) having a fixed shape.

Though this asymptotic estimate may not be a strict bound, we believe that the logarithmic factor should not be present in (42). On the other hand, for the case without spherical symmetry we know that the asymptotic estimate cannot be an upper bound, for, by taking \( N \) distant potential wells saturating separately the inequality with \( I = 1 + \varepsilon \), it is possible to build a system with \( N \) bound states. The best one can hope to prove is therefore

\[ N \leq I \]

At present we only know that this inequality holds for \( I = 1 \) and also for \( I = 2 \). It holds for \( I = 2 \) for, if we have two bound states, the wave function of the higher state cannot have a constant sign since it is orthogonal to the ground state, which has a positive definite wave function. Therefore the space is divided at least into two regions where \( \psi > 0 \), \( \psi < 0 \), with \( \psi \) vanishing on the border. Our inequalities can be applied to these two regions separately. This gives the factor 2.

4. MUONIC ATOMS

As a simple illustration of the use of no-binding theorems, we shall derive bounds for the ground-state energy \( E_0 \) of an atom with a \( \mu^- \) and \( N \) electrons. We shall take the nuclear charge \( Z \) sufficiently small so that relativistic and nuclear size effects can be neglected. Naively one would assume that the electrons just see \( Z - 1 \) and thus one should get (in the atomic unit):

\[ E_0 = \frac{Z^2 \mu}{2} + E(N,Z-1) \]

(i.e. the energy of the muon in its ground state)  

(i.e. the energy of \( N \) electrons in the potential of a charge \( Z - 1 \)).

It is trivial to see\(^{10}\) that this represents an upper bound for the exact energy. To prove a certain accuracy of this naive expectation we shall derive a lower bound near by. Designating the muon variables by \( (x, p) \) and those of the electrons by \( (x_i, p_i) \), \( i = 1, \ldots, N \), we can write the total Hamiltonian

\[ H = H_0 + \sum_{i=1}^{N} V_i \]

\[ H_0 = \frac{p^2}{2\mu} + \sum_{i=1}^{N} \frac{k_i^2}{2} - Z \left( |x|^2 + \sum_{i=1}^{N} |x_i|^2 \right) + \sum_{i>j} |x_i - x_j|^{-1} \]  

\[ V_i = |x - x_i|^{-1} > 0 \]  

(44)
To obtain lower bounds we shall employ the projection method
\begin{equation}
H \geq H_0 + \sum_i P (P_i V_i^{-1} P) P
\end{equation}
where \( P \) is the projector onto the ground state of the muon \((r, r_i = |\hat{x}|, |\hat{x}_i|)\), and \( V_i^{-1} \) is the inverse of \( V_i \) in configuration space:
\begin{equation}
P = \left[ 2 (z_\mu)^2 e^{-z_\mu r} \right] \left[ 2 (z_\mu)^2 e^{-z_\mu r} \right]^{-1}
\end{equation}

\begin{equation}
P (P | x-x_i | P)^{-1} P = \frac{1}{r_i} - \frac{1}{r_i} \left[ 1 + \frac{z_\mu^2 r_i^2}{1-e^{-2z_\mu r_i}(1+2z_\mu)} \right]^{-1}
\end{equation}

Since
\begin{equation}
H_0 \geq \left[ -\frac{z_\mu^2}{2} + \sum \frac{1}{2} \sum r_i \sum r_i^{-1} + \sum \|x_i-x_i\|^{-2} \right] P
\end{equation}

we have the operator inequality
\begin{equation}
H \geq \left[ -\frac{z_\mu^2}{2} + \sum \frac{1}{2} \sum r_i \sum r_i^{-1} + \sum \|x_i-x_j\|^{-2} \right] P
\end{equation}

\begin{equation}
+ (1-P) \left[ -\frac{z_\mu^2}{2} + E(N, z) \right] + P \left\{ \sum \left( \frac{1}{2} \sum r_i \sum r_i^{-1} + V(r_i) \right) \right\}
\end{equation}

Now
\begin{equation}
\left\{ \frac{1}{2} \right\} \geq 0
\end{equation}

if
\begin{equation}
\frac{2m_i}{z_\mu^2} < \frac{1}{P-1} \left[ \frac{1}{r(2p)} \right] \int [U^{-p+1} r^{-1}] \, dr
\end{equation}

with
\begin{equation}
U = \left[ 1 + \frac{z_\mu^2}{1-e^{-2z_\mu}(1+\frac{z_\mu^2}{2})} \right]^{-1}
\end{equation}

for some value of \( p \).

The maximum of the right-hand side is reached for
\begin{equation}
p = 1.8242, \quad \frac{2m_i}{z_\mu^2} = 1.2706
\end{equation}

Thus using scaling in the distances, we get the inequality,
\begin{equation}
-\frac{z_\mu^2}{2} + \left( 1 - \frac{1.5\times 4}{z_\mu^2} \right)^{-1} E(N, z-1) \langle E \rangle \langle E \rangle \langle -\frac{z_\mu^2}{2} + E(N, z-1) \rangle
\end{equation}
which holds as long as the left-hand side is smaller or equal to
\[-\frac{Ze^4}{2} + E(N,Z)\]
provided
\[\frac{Ze^4}{2m_1} > 1.574.\]

However, from scaling we easily get
\[E(N,Z) > \left(\frac{Ze^4}{2(Z-1)^2}\right)\frac{E(N,Z-1)}{2}.\]  \hspace{1cm} (53)

Hence the inequality holds if
\[|E(N,Z-1)| \left[\left(\frac{Z}{Z-1}\right)^2 - \left(1 - \frac{1.574}{Z}\right)^{-1}\right] < \frac{3}{8} \frac{Z^2 \mu}{\mu_1} \]

Even the crudest upper bound on \(|E(N,Z-1)|\) shows that for \(\mu \geq 1\) this inequality is always satisfied.

Thus we see that the uncertainty in the electron energy is always less than 1%, and with increasing \(Z\) soon becomes smaller than the relativistic corrections.

Another by-product is that we prove at the same time that a system composed of a proton, an electron, and a particle of negative charge is not bound if the mass of this particle is larger than 1.574 electron masses. Notice that if one solves the Schrödinger equation numerically for the potential \(v\), the figure 1.574 is replaced by 1.570!

Acknowledgements

This work was done while we were studying a broader subject in collaboration with Elliott Lieb and Jack Barnes. We acknowledge many stimulating exchanges with them. We thank B. Bonnier for help in computing and H. Epstein for discussions.
Table 1

<table>
<thead>
<tr>
<th>Potential</th>
<th>Exact</th>
<th>Bargmann bound</th>
<th>$p = \frac{3}{2}$</th>
<th>Optimal $p$</th>
<th>Optimal $V$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Square well $ V \theta [1-r] $</td>
<td>$V = 2.467$</td>
<td>$V = 2$</td>
<td>$V = 2.108$</td>
<td>$1.1764$</td>
<td>$2.359$</td>
</tr>
<tr>
<td>Exponential $ V \exp (-2r) $</td>
<td>$V = 5.783$</td>
<td>$V = 4$</td>
<td>$V = 5.669$</td>
<td>$1.4473$</td>
<td>$5.753$</td>
</tr>
<tr>
<td>Yukawa $ \frac{V \exp -r}{r} $</td>
<td>$V = 1.680$</td>
<td>$V = 1$</td>
<td>$V = 1.648$</td>
<td>$1.6875$</td>
<td>$1.664$</td>
</tr>
<tr>
<td>Gaussian $ V \exp (-r^2) $</td>
<td>$V = 2.684$</td>
<td>$V = 2$</td>
<td>$V = 2.615$</td>
<td>$1.336$</td>
<td>$2.660$</td>
</tr>
</tbody>
</table>
We want to prove
\[ \int |\nabla \psi_R|^2 \, d^3 x \leq \int |\nabla \psi|^2 \, d^3 x \] (A.1)
and in fact, more generally
\[ \int_{\psi_R > M} |\nabla \psi_R|^2 \, d^3 x \leq \int_{\psi > M} |\nabla \psi|^2 \, d^3 x \] (A.2)
we define
\[ I(M) = \int_{\psi > M} |\nabla \psi|^2 \, d^3 x \] (A.3)
\[ I_R(M) = \int_{\psi_R > M} |\nabla \psi_R|^2 \, d^3 x \] (A.4)

We repeat that, by definition \(^{11,12}\),

i) \( \psi_R \) is a decreasing function of \( r = |x| \);

ii) \[ \int_{\psi > M} d^3 x = \int_{\psi_R > M} d^3 x = V(M) \] (A.5)

(the domain of integration of the left-hand side is not necessarily connected).

We call \( d\sigma_M \) the (scalar) surface element of the surface \( \psi = M \) and \( d\sigma_{MR} \) the surface element of the surface \( \psi_R = M \). Notice that \( \nabla \psi \) is normal to the surface \( \psi = M \) and \( \nabla \psi_R \) normal to the surface \( \psi_R = M \). Then differentiating (A.5) we get
\[ \left| \frac{dV}{dM} \right| = \int \frac{d\sigma_M}{|\nabla \psi|} = \int \frac{d\sigma_{MR}}{|\nabla \psi_R|} \] (A.6)

and differentiating (A.3) and (A.4)
\[ \left| \frac{dI}{dM} \right| = \int |\nabla \psi| \, d\sigma_M \] (A.7)
\[ \left| \frac{dI_R}{dM} \right| = \int |\nabla \psi_R| \, d\sigma_{MR} \] (A.8)
multiplying (A.7) and (A.8), we get
\[ \left| \frac{dV}{dM} \right| \left| \frac{dI}{dM} \right| = \left( \int \frac{d\sigma_M}{|\nabla \psi|} \right) \left( \int |\nabla \psi| \, d\sigma_M \right) \geq \left( \int d\sigma_M \right)^2 \] (A.9)
by Schwarz's inequality, while
\[ \left| \frac{dV}{dM} \right| \left| \frac{dI}{dM} \right| = \left| \int \frac{d\sigma_{MR}}{|\nabla \psi_r|} \right| \left| \nabla \psi_r \right| d\sigma_{MR} = \left| \int d\sigma_{MR} \right|^2 \] (A.10)

Here the equality sign comes from the fact that $|\nabla \psi_r|$ is constant, by construction, along the surface $\psi = \text{const}$. Now the surfaces $\psi = M$ and $\psi_R = M$ contain by (A.5) the same volume. By standard isoperimetric inequalities we know that the minimal surface for a given volume is a sphere. Hence
\[ \int d\sigma_M \geq \int d\sigma_{MR} \] (A.11)

and
\[ \left| \frac{dV}{dM} \right| \left| \frac{dI}{dM} \right| \geq \left| \frac{dV}{dM} \right| \left| \frac{dI}{dM} \right| \] (A.12)

and
\[ \left| \frac{dI}{dM} \right| \geq \left| \frac{dI_R}{dM} \right| \] (A.13)

Then (A.1) follows by integration of (A.13) from $M = 0$ to $M = \text{maximum of } \psi$.

There are several subtleties that we have ignored in this proof. For instance we have assumed that there are no three-dimensional regions where $\psi$ is constant. We have assumed that the regions $\psi = \text{const}$ are two-dimensional surfaces made of a finite number of pieces, sufficiently smooth, etc. We leave it to specialists to make this proof completely clean. Notice also that the proof works in any number of dimensions.

An alternative proof, avoiding the use of isoperimetric inequalities and using the Green's function of the diffusion equation, has been proposed by Elliott Lieb\(^{13}\).
This Appendix is devoted to the proof of Theorem 2. What we have to show is that the formal calculations leading to the functions (28) and the numbers \( v_k \) (29) indeed furnish the true "ground state" resp. the true minimum of the functional \( G_k(\phi) \) (23).

To start with, let us remark that the functional (23) \( G(\phi) = I/J^{1/q} \) (we work with a fixed \( 2 < 2q = k < \infty \) so we omit from now on any indices referring to this number) is a priori meaningful on a space of functions \( \phi \) on which the integrals \( I \) and \( J \) converge. The largest such space is the Banach space \( \beta \) of functions with finite norm

\[
N^*(\phi) = I(\phi) + J^{1/q}(\phi).
\]  
(B.1)

\( \beta \) can be regarded as the completion of the space \( \gamma = \{ C^\infty \text{ functions with compact support} \} \) with respect to the norm \( N \).

The trouble with the functional \( G \) is that it is translationally invariant, so that if a ground state exists it is necessarily infinitely degenerate: if \( \phi \) minimizes \( G \) then so do all the functions \( \phi_{\lambda,a}(x) = \lambda \phi(x-a) \) \( \phi \) cannot be translationally invariant since for \( \phi = \text{const} N(\phi) = \infty \); this is therefore a case of "broken symmetry"]. The idea of the proof is the following: we shall break this invariance by first considering the case of a compact interval, say \( K = [-R, +R] \), \( 0 < R < \infty \). For the corresponding functional \( G_K(\phi) \) we shall then easily prove the Lemma 1:

a) There exists a function \( \phi \in \mathcal{K} \) which minimizes the functional, where \( \mathcal{K} \) is the Hilbert space of (real-valued) functions on \( K = [-R, +R] \) obtained by completion of \( \mathcal{H}(K) \) with respect to the norm

\[
N_2^*(\phi) = \int_K (|\phi|^2 + \frac{1}{4} |\phi|^2) \, dx \equiv \|\phi\|^2_2 + \frac{1}{4} \|\phi\|^2_2.
\]  
(B.2)

b) The minimizing function is at least twice continuously differentiable on \( K \) and satisfies there the differential equation (24) and the boundary condition

\[
\phi(-R) = \phi(R) = 0
\]  
(B.3)

which determine \( \phi \) uniquely up to a multiplicative constant. The corresponding minimal value \( v(R) = G_K(\phi) \) is strictly positive.

Theorem 2 will then follow from this lemma by taking the limit \( R \to \infty \) if we notice that

\[
G_K(\phi) = G(\phi) \quad \text{for} \quad \phi \in \mathcal{D}(K)
\]  
(B.4)
Because of the density of $\mathcal{D}(K)$ in $\mathcal{C}_K$ and of $\mathcal{D}(\mathbb{R})$ in $\mathcal{B}$, it follows from $\mathcal{D}(K_1) \subset \mathcal{D}(K_2) \subset \mathcal{D}(\mathbb{R})$ when $K_1 \subset K_2$ that the function

$$
\nu(R) = \inf_{\phi \in \mathcal{D}(K)} G_K(\phi) = \inf_{\phi \in \mathcal{D}(K)} G_K(\phi) > 0
$$

is a decreasing function of $R$ and that

$$
\lim_{R \to \infty} \nu(R) = \nu = \inf_{\phi \in \mathcal{D}(\mathbb{R})} G(\phi) = \inf_{\phi \in \mathcal{B}} G(\phi) \quad (B.5)
$$

A direct computation of this limit will turn out to coincide with the value $\nu$ given in the text, where we have shown that this value is attained by the function $(28)$. It is then easy to see that up to translations and multiplication by a constant, this solution is unique.

**Proof of Lemma 1:** Let us first remark that the space $\mathcal{C}_K$ consists of continuous functions on $K$ vanishing at both ends of $K$, for which the norm $N_2$ is finite. This automatically ensures the existence of the integral $J(\phi)$, so that $G_K$ is meaningful for all $0 \neq \phi \in \mathcal{C}_K$. Indeed for any $\phi \in \mathcal{D}(K)$ the Schwarz inequality gives

$$
|\phi(x_1) - \phi(x_2)| \leq \int_{x_1}^{x_2} \phi'(x) dx \leq |x_1 - x_2| \sqrt{N_2(\phi)} \quad (B.6)
$$

where $x_1$, $x_2$ are any two points in $K$. Also by setting $x_1 = x$ and $x_2 = \pm R$ we get from here in view of $\phi(\pm R) = 0$

$$
|\phi(x)| \leq \min |x \pm R| \sqrt{N_2(\phi)} = \chi(x) N_2(\phi) \quad (B.7)
$$

If we take now a Cauchy sequence $\phi_n \in \mathcal{D}(K)$ which converges to an arbitrary element $\phi \in \mathcal{C}_K$ in the norm $N_2$, it follows that (B.6) and (B.7) are valid also for any element of $\mathcal{C}_K$.

By the very definition of $\nu(R)$ there exists a sequence of $0 \neq \phi_n \in \mathcal{D}(K)$ such that $G_K(\phi_n) \to \nu(R)$ for $n \to \infty$. Since $G_K$ is scale-invariant we may normalize the $\phi_n$ so that

$$
J(\phi_n) = 1 \quad \text{and hence} \quad I(\phi_n) = N_2(\phi_n)^2 \equiv v_n \nu(R) \quad (B.8)
$$

The inequalities (B.7) and (B.8) tell us that the family of functions $\{\phi_n\}_{n=1}^{\infty}$ is equi-continuous and uniformly bounded. The Arzela-Ascoli theorem tells us that this family is compact in the sup-norm, so that we may assume that the sequence $\phi_n$ converges uniformly on $K$ to the $\frac{1}{2}$-Hölder continuous function $\phi(x)$ bounded by $\nu(R)$. Because of uniform convergence, we have

$$
1 = \lim_{n \to \infty} J(\phi_n) = J(\phi), \quad (B.9)
$$
so that \( \phi \neq 0 \). We have to show that \( \phi \in \mathcal{C}_K \) and \( G_K(\phi) = \nu(R) \).

Because of uniform convergence we see that the sequence \( \sigma_n = \frac{1}{n} \int_K \phi_n^2 \, dx \) converges to a strictly positive limit:

\[
\lim_{n \to \infty} \sigma_n = \frac{1}{n} \int_K \phi_n^2 \, dx = \sigma > 0 \tag{B.10}
\]

This implies also the convergence of the sequence:

\[
\rho_n = \int_K \phi_n^2 \, dx = \nu - \sigma_n \to \rho > 0 \tag{B.11}
\]

If we denote by \( (u, v) \) the scalar product \( \int_K uv \, dx \), then for any \( v \in \Theta(K) \) the limit

\[
\lim_{n \to \infty} (\phi_n', v) = - \lim_{n \to \infty} (\phi_n, v') = - (\phi, v') = (\phi', v) \tag{B.12}
\]

exists again because of uniform convergence. Hence the derivative \( \phi' \) of \( \phi \) exists in the sense of distributions as indicated by the last expression in (B.12). On the other hand,

\[
|\langle \phi_n', v \rangle| \leq \| \phi_n' \|_2 \| v \|_2 = \rho_n^{1/2} \| v \|_2^{1/2}.
\]

By taking the limit \( n \to \infty \) we find that the linear functional (B.12) is bounded by

\[
|\langle \phi', v \rangle| \leq \rho^{1/2} \| v \|_2^{1/2} \text{ for all } v \in \Theta(K). \tag{B.13}
\]

Because \( \Theta \) is dense in \( L_2(K) \) with scalar product \( (u, v) \), the linear functional \( (\phi', v) \) can be uniquely extended to the whole of \( L_2 \). By the Fischer-Riesz theorem there exists a \( w \in L_2 \) such that \( (\phi', v) = (w, v) \). Hence \( \phi' = w \in L_2(K) \) and thus \( \phi \in \mathcal{C}_K \). By putting \( v = \phi' \) in (B.13) we further obtain \( (\phi', \phi') < \rho \). Combining all these results we get the inequality

\[
G_K(\phi) \leq \rho + \sigma = \nu(R)
\]

But since \( \nu(R) \) was supposed to be the infimum of \( G_K \) on \( \mathcal{C}_K \), the equality sign must hold:

\[
G_K(\phi) = \nu(R) > 0 \tag{B.14}
\]

It remains only to show that the \( \phi \) we have obtained is twice continuously differentiable and satisfies the differential equation (24):

\[
\phi'' = \frac{1}{4} \phi - \chi(\phi^{4-\varepsilon}(\phi) \equiv L(\phi), K = I/I > 0 \tag{B.15}
\]

As is usual in the variational calculus, it follows immediately from the observation that the function \( \lambda \to G_K(\phi + \lambda v) \) takes its absolute minimum at \( \lambda = 0 \) for all \( v \in \Theta(K) \). Here \( \phi'' \) has to be understood in the sense of distributions, but since the right-hand side \( L(\phi) \) has been proved to be continuous, the second derivative
exists also in the ordinary sense (after having maybe changed the $L^2$-function $\phi'$ on a set of Lebesgue measure zero). Finally, the initial condition (B.3) holds for any element of $\mathcal{H}$ since $\chi(\pm R) = 0$ in the inequality (B.7). This completes the proof of our lemma.

We now have to compute the number $v(R)$. The first integral of Eq. (B.15) is given by

$$ \phi' = \frac{1}{4} \phi^2 - \frac{2}{\kappa^2} |\phi| + C \equiv P(\phi) \quad (B.16) $$

The initial condition (B.3) implies that $c = \phi'^2(\pm R) = \phi'^2(-R)$, which is a strictly positive number, since $\phi(R) = \phi'(-R) = 0$ would imply $\phi \equiv 0$. The solutions of (B.16) are obtained as the inverse functions of the multivalued integral

$$ x = \pm \int \frac{d\phi}{\sqrt{P(\phi)}} \quad (B.17) $$

The strict positivity of the constants $\kappa$, $C$ and $k > 2$ implies, as is easily seen, that the function $P(t) = \frac{1}{4}t - (2\kappa/k)t^k + C$ has exactly one simple zero $t_0 > 0$ for $t \geq 0$. Hence $P(\phi) > 0$ for $-\phi_0 < \phi < \phi_0$, $\phi_0 = t_0^{\frac{1}{2}}$, it has a simple zero at $\phi = \pm \phi_0$ and is negative elsewhere. As it is well known from the theory of the pendulum, this implies that the inverse functions of (B.17) (which differ from each other only by a translation) are periodic functions defined on the whole real line that oscillates between the extremal values $\pm \phi_0$; their simple zeros are half a period apart and they monotonically increase resp. decrease between two consecutive extremal values. The property $P(-\phi) = P(\phi)$ furthermore implies that they are symmetric with respect to their extremal points and antisymmetric with respect to their zeros.

It is convenient to normalize $\phi_0 = 1$ by a change of scale $\phi \rightarrow \lambda \phi$. With this normalization

$$ \lambda = \frac{2x}{\kappa} - \frac{1}{4} > 0 \quad \text{which implies} \quad x > \frac{\kappa}{8} \quad (B.18) $$

The quarter-period of the solutions of (B.16) is given by

$$ T(x) = \int_0^x \frac{dt}{\sqrt{P(t, x)}} \quad (B.19) $$

$\phi(\pm R) = 0$ imposes the condition

$$ T(x) = R/m , \quad m = 1, 2, 3 \ldots \quad (B.20) $$

which can always be solved for $\kappa$

$$ \kappa_n = T^{-1}(R/m) \quad (B.21) $$
$T$ is namely a strictly decreasing real-analytic function of $\kappa$ for $\kappa > k/8$, and moreover
\[
\lim_{x \to \infty} T(x) = 0 \quad \lim_{x \to k/8} T(x) = \infty.
\] (B.22)

[The last statement comes from the logarithmic divergence of the integral (B.19) at $t = 0$ for $\kappa = k/8$.] Hence $T^{-1}$ exists on $(0, \infty)$, is real-analytic and strictly decreasing, and satisfies:
\[
\lim_{R \to 0} T^{-1}(R) = \infty \quad \lim_{R \to \infty} T^{-1}(R) = k/8.
\] (B.23)

This discussion shows that the functional $G_K$ has a denumerable infinity of "stationary states" $\phi_n$ $(n = 1, 2, 3, \ldots)$, the $n^{th}$ of which has exactly $n - 1$ distinct zeros in the interior of $K$. It is expected that $\phi = \phi_1$ is the sought-for ground state. To show this, we compute $G_K(\phi_n)$. By multiplying the differential equation (B.15) for $\phi_n$ by $\phi_n$ and integrating, we obtain, because of $\phi(\pm R) = 0$:
\[
I(\phi) = \kappa J(\phi),
\] and hence
\[
\tau_n = \gamma_n = \frac{1}{2\pi} \int_0^{2\pi} \frac{1}{\sqrt{p(t)}} dt.
\]
(Equation B.24)

In the last step we have used the fact that $(-R, +R)$ contains exactly $2n$ quarter-periods of $\phi_n$, and we made the change of variables $dx = P^{-1}(t) dt$ on the quarter-period. Here $p^{-1} = 1 - 2\kappa^{-1}$. It turns out that $L(\kappa)$ is a strictly monotonically increasing function of $\kappa$ for $(k/8) < \kappa < \infty$ and since $\kappa_n$ increases with $n$ according to (B.21), the ground state indeed corresponds to the value $n = 1$. We now define, for $n \geq 2$, $\psi_n = \phi_n^\ast$ on the last half period $[R - (2/n)R, R]$, $\psi_n = 0$ elsewhere. Evidently $\psi_n \in H_K$ and $G_K(\psi_n) = L^{-1}(\psi_n) < G_K(\phi_n)$, so that $\phi_n$ cannot be the ground state of $G_K$. Neither can $\psi_n$, since its derivative has a discontinuity at $x = \pm R(1 - 2/n)$, which contradicts Lemma 1. Hence $\phi_1$ is the minimizing function determined uniquely up to a multiplicative constant and
\[
\psi(R) = L^{1/2}(\kappa) \quad \text{where} \quad \kappa = T^{-1}(R),
\] (B.25)

From (B.23) it follows that $\lim R \to 0$ corresponds to $\lim \kappa = k/8$, and we readily see that formula (24) of Section 2 is obtained in this limit. This proves formula (20) of Theorem 2. That the functions (28) saturate this lower bound we have shown in the text. Their uniqueness comes from the following argument. As in the proof of Lemma 1, it follows from inequality (B.6) (which holds also for all $\phi \in B$ on which the functional $G$ is defined) that any function $\phi$ minimizing $G$
also satisfies the differential equation (B.15). Its first integral is given by (B.16) with \( C = 0 \), because there must exist a sequence of points \( x_n \to \infty \) such that \( \lim \phi(x_n) = \lim \phi'(x_n) = 0 \) [otherwise the integral \( I(\phi) \) would diverge]. But all solutions of the last equation are given by (28), as shown in the text. This completes the proof of Theorem 2.

**Note:** It is interesting to remark that the functional \( G_\mathbb{H} \) of a half-infinite interval, say \( \mathbb{H} = (-\infty, 0) \), has the same infimum \( \nu \) as the functional \( G \) of the whole real line. On the one hand we have namely \( \inf G_\mathbb{H} \geq \nu \), on the other hand one easily sees that \( \lim_{n \to \infty} G_\mathbb{H}(\phi_n) = \nu \) for the sequence of functions \( \phi_n(x) = \alpha(x) \phi_q(x + n) \), where \( \phi_q \) is a minimizing function (28) of the functional \( G \) and \( \alpha \) is any positive \( C^\infty \)-function such that \( \alpha(x) = 0 \) for \( x \geq 0 \); \( 0 \leq \alpha \leq 1 \) for \( -1 \leq x < 0 \) and \( \alpha = 1 \) for \( x < 1 \). The infimum is, however, not attained. For suppose some \( \phi \in \mathcal{H}_x \) does minimize \( G_\mathbb{H} \), then it must be a solution of (B.16) with \( C = 0 \). Since no solution of this equation vanishes at \( x = 0 \), \( \phi \notin \mathcal{H}_x \). This proves the remark made at the end of Section 2.
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