On the Energy Levels of the Hydrogen Atom

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Abstract

We re-examine the justification for the imposition of regular boundary conditions on the wavefunction at the Coulomb singularity in the treatment of the hydrogen atom in non-relativistic quantum mechanics. We show that the issue of the correct boundary conditions is not independent of the physical structure of the proton. Under the physically reasonable assumption that the finite size and structure of the proton can be represented as a positive correction to the Coulomb potential, we give a justification for the regular boundary condition, which, in contrast to the usual treatments, is physically motivated and mathematically rigorous. We also describe how irregular boundary conditions can be used to model non-positive corrections to the Coulomb potential.

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1 Introduction

One of the unsatisfactory features of Old Quantum Theory was the primacy of the concept of ‘quantum number’, which does not arise from more basic physical principles thereby leaving a certain mystery as to the true origin of discreteness in quantum theory and the distinguished nature of the positive integers. It was to remove this limitation that Schrödinger embarked upon a programme of recasting quantisation as an eigenvalue problem, studying the hydrogen atom as his first example [1].

Of course, eigenvalue problems such as those encountered in quantum theory require the specification of boundary conditions in order to be well-posed. In the hydrogen atom case, there is a particular issue about what boundary conditions should be imposed on the wavefunction at the Coulomb singularity. This was understood by Schrödinger, who imposed that the wavefunction be finite. With this condition, the negative energy eigenvalues of the idealised Coulomb Hamiltonian precisely replicate the Bohr levels, a success which confirmed the validity of the new approach. As Schrödinger wrote [1]

The essential thing seems to me to be, that the postulation of “whole numbers” no longer enters into the quantum rules mysteriously, but that we have traced the matter a step further back, and found the “integralness” to have its origin in the finiteness and single-valuedness of [the wavefunction]

But is finiteness of the wavefunction an axiom of quantum mechanics? Although this issue is often considered in quantum mechanics textbooks, there does not appear to be a satisfactory treatment in the literature – see [2] for a discussion of the usual treatments. In the present paper, we examine this problem in detail for the particular case of the hydrogen atom. One of our main aims will be to provide a physically motivated and mathematically rigorous justification for the condition that the wavefunction should be finite at the Coulomb singularity. We shall also consider the interpretation of other possible boundary conditions as models for nuclear structures differing greatly from that of the physical proton.

Our general methodology, which is discussed at length in [2], starts from the distinction introduced in [3] between true problems and idealised problems. In a true problem, interactions are modelled by a smooth potential in the Schrödinger equation, reflecting our expectation that only smooth potentials occur in nature. In the case of the hydrogen atom, one can identify a class of true problems consisting of models in which the finite size and structure of the proton is modelled by a smooth potential which deviates from the Coulomb form within the nuclear radius, ‘rounding off’ the Coulomb singularity. For simplicity, we shall mainly consider spherically symmetric potentials of this form, but we make no other restriction on our class of true problems. For true problems, we will take finiteness and smoothness of the wavefunction to be axiomatic for quantum mechanics.
Idealised problems represent limiting cases of true problems. As such, they can possess distinguished points at which some of the structure of a more fundamental true problem has been simplified. In the case of the hydrogen atom, the Coulomb singularity is a distinguished point, for it represents the physical proton of the true problem. Note that the idealised problem need not be singular at such points. For example, a true problem in which the potential changes steeply but smoothly from one value to another could be idealised by a potential step. One might idealise a true problem with a potential compactly supported within a small neighbourhood of the origin, by an idealised problem with no potential at all, but with the origin as a distinguished point (see [3], where this case is treated in depth). At such distinguished points in idealised problems, boundary conditions can only be physically justified by reference to the true problem one intends the idealisation to represent.

Accordingly, in Section 2, we determine the class of allowed idealised problems for the case in hand by considering limits (in the strong resolvent sense [15]) of sequences of Hamiltonians for true hydrogen atom problems whose ‘nuclear radii’ tend to zero. We thereby determine a 1-parameter family of idealised problems with different boundary conditions at the Coulomb singularity, all of which correspond to the limiting behaviour of true problems from our class. The spectra of these idealised problems can differ markedly in the S-wave, although for higher angular momenta, all idealisations yield the Bohr levels.

Clearly, in order to justify the choice of regular boundary condition at the origin (the unique choice leading to the Bohr levels in the S-wave) we must make further restrictions on our class of true problems. In Section 3, we make the physically reasonable restriction to true problems whose potentials represent positive corrections to the Coulomb potential localised within a small nuclear radius. Under these assumptions, we prove that the true problem has energy levels which differ only slightly from those of the idealised system with the regular boundary condition (i.e. the Bohr levels). There are, of course, well known estimates from first order perturbation theory of the finite size corrections to the Bohr levels under the further assumption that the nucleus is a smooth positive charge distribution. However, our treatment will cover a wide class of nuclear models in a non-perturbative fashion. We also note that this argument is not usually given as the ‘correct’ understanding of the point in question. We will also show that there exist true problems with arbitrarily small nuclear radius (with non-positive corrections to the Coulomb potential) whose S-wave energy levels differ greatly from the Bohr levels.

We also provide a second justification by considering limits in the sense of strong resolvent convergence of sequences of true problem Hamiltonians whose nuclear radii tend to zero, interpreting this as a means of ‘regularising’ the point charge. By definition, in the general case, the class of possible self-adjoint limits is precisely the class of idealised problems, which (as we mentioned above) is a 1-parameter family of operators with different boundary conditions at the ori-
gin. However, restricting to regularisations which can be modelled by positive, compactly supported corrections to the Coulomb potential, we will prove that all such regularisation schemes converge rigorously to the idealised Hamiltonian with regular boundary conditions.

In Section 4, we turn to the interpretation of irregular boundary conditions at the Coulomb singularity, by developing a scattering length formalism for systematically matching any given true problem to its ‘best fit’ idealisation. This formalism also plays a rôle in the proof of our convergence theorems mentioned above. In Section 5, we examine the situation for angular momenta \( \ell \geq 1 \). We find that the Bohr spectrum in these sectors is more stable against finite size effects than in the S-wave. Section 6 contains the rigorous proofs of some of the results stated in earlier sections.

One of the motivations for this work was the recent study undertaken by Kay and the author of the rôle of model dependence in systems which interact with small objects \([3]\), and in particular the ‘principle of sensitivity’ introduced in \([3]\) (see also \([4]\)) which relates the range of possible large scale (low energy) behaviour of a class of true problems to the range of possible behaviour exhibited by the corresponding class of idealised problems. We conclude in Section 7, by discussing the relation of our present results to the principle of sensitivity, with which we find good agreement.

\section{True and Idealised Problems}

The Hamiltonian corresponding to the idealised hydrogen problem is given as a differential operator by

\[
H_{\text{ideal}} = -\Delta + \frac{\gamma}{r},
\]

where we employ units in with \( \hbar = 4\pi \epsilon_o = 1 \) and in which the reduced mass of the electron is set to \( \frac{1}{2} \) (\( \gamma \) is negative). The Bohr radius is thus given by \( a_0 = 2/|\gamma| \). Our Hilbert space of wavefunctions is \( \mathcal{H} = L^2(\mathbb{R}^3, d^3r) \) with inner product denoted \( \langle \cdot | \cdot \rangle \). To define \( H_{\text{ideal}} \) rigorously on \( \mathcal{H} \), we must specify its domain, which inevitably begs the question of the appropriate boundary conditions at the Coulomb singularity. In order to circumvent this, we consider the class of true problems, in which the singularity is rounded off within some nuclear radius, and for which we assume finiteness of the wavefunction as an axiom. We then define the class of idealised Hamiltonians to consist of the self-adjoint limits in the strong resolvent sense of sequences of true problem Hamiltonians whose nuclear radii tend to zero.

Let \( V \) be the class of all measurable real-valued functions \( V(r) \) on \( \mathbb{R}^+ \) compactly supported within some radius of the origin such that \( r \mapsto \frac{\gamma}{|r|^{-1}} + V(|r|) \) is smooth on \( \mathbb{R}^3 \). Then the class of true problems consists of all Hamiltonians
defined as the closure of an operator of form
\[ -\Delta + \frac{\gamma}{r} + V(r) \quad \text{on} \quad C_0^\infty(\mathbb{R}^3) \subset \mathcal{H} \]  
for \( V \in \mathcal{V} \). We refer to the radius of support of \( V \) as the nuclear radius. Operators of form (2.2) are automatically essentially self-adjoint as a consequence of the Kato-Rellich theorem by hypothesis on \( \mathcal{V} \) (see Theorem X.15 in [16]). This definition encodes two desirable features of true problems: firstly that only smooth potentials occur in nature, and secondly that the wavefunction is everywhere finite. The latter follows from our choice of domain, which has already injected regular boundary conditions at the origin.

We now define the class \( \Sigma \) of all sequences of true problem Hamiltonians \( H_n = -\Delta + \gamma/r + V_n(r) \) whose nuclear radii (i.e. the radii of the supports of the \( V_n \) about the origin) tend to zero. Our idealisations are the self-adjoint limits of such sequences in the strong resolvent sense.

The following result, which we prove in Section 6, classifies the idealised Hamiltonians as the self-adjoint extensions of the symmetric operator \( H_{\text{ideal}} \) on the domain \( C_0^\infty(\mathbb{R}^3\setminus\{0\}) \).

**Theorem 2.1** Let \( H_{\text{ideal}} = -\Delta + \gamma/r \) on \( C_0^\infty(\mathbb{R}^3\setminus\{0\}) \). (a) Let \( \{H_n\} \in \Sigma \). If \( \{H_n\} \) has a self-adjoint limit \( H \) in the strong resolvent sense, then \( H \) is a self-adjoint extension of \( H_{\text{ideal}} \). (b) Furthermore, all self-adjoint extensions of \( H_{\text{ideal}} \) arise as the strong resolvent limits of sequences in \( \Sigma \).

We note that these extensions have also been exhibited as limits of sequences of self-adjoint operators by Albeverio and co-workers [5], where however, the convergence is in the norm resolvent sense. We motivate our choice of convergence by two observations. Firstly, the strong resolvent convergence of a sequence of self-adjoint Hamiltonians to a self-adjoint limit is equivalent (Trotter’s Theorem [15]) to the statement that
\[ e^{iH_n t} \psi \to e^{iH t} \psi \quad \text{for all} \ t, \ \text{and all} \ \psi \in \mathcal{H}. \]  
Thus strong resolvent convergence is a natural candidate for the notion of dynamical convergence. Under certain circumstances, it can be shown that if \( H_n \to H \) in the strong resolvent sense, then the corresponding Møller wave operators \( \Omega^\pm(H_n, H_o) \) converge strongly to \( \Omega^\pm(H, H_o) \), where \( H_o \) is a suitable comparison dynamics [3].

Secondly, the spectrum can contract in the limit of strong resolvent convergence (although it cannot expand) in contrast to norm resolvent convergence, in which the spectrum can neither contract nor expand. (See Theorem VIII.24(a) and the following discussion in [13].) This property of strong resolvent convergence will be important in the sequel; furthermore norm resolvent convergence is too strong for our purposes: one can see that there are no analogues of some of our results in this sense of convergence.
We also note that the results in [5] concern sequences of scaled Hamiltonians, whereas (due to our weaker notion of convergence) we are not restricted in this way. In addition, the scattering length formalism developed in Section 4 provides a transparent physical interpretation for our convergence results. In [3] these differences are discussed at greater length in the case of short range (non-Coulombic) potentials.

We quickly review the classification of the self-adjoint extensions of $H_{\text{ideal}}$ along the lines of the discussion in [5]. The deficiency indices $n^\pm$ of $H_{\text{ideal}}$ are defined to be the dimensions of the deficiency subspaces $W^\pm = \ker(H^*_{\text{ideal}} \mp i)$, i.e. the number of independent $L^2$ solutions to

$$
H^*_{\text{ideal}} \psi = \pm i \psi. \tag{2.4}
$$

$H^*_{\text{ideal}}$ may be seen to act ‘classically’ (cf. Proposition 2 in the appendix to section X.1 of [16]) i.e. such that any such solution solves

$$
(-\Delta + \frac{\gamma}{r}) \psi = \pm i \psi \tag{2.5}
$$

as a differential equation, and so usual techniques of partial differential equations suffice. In the familiar way, we use the decomposition

$$
L^2(\mathbb{R}^3, d^3 r) = \bigoplus_{\ell=0}^{\infty} L^2(\mathbb{R}^+, r^2 dr) \otimes K_{\ell} \tag{2.6}
$$

where $K_{\ell}$ is the subspace of $L^2(S^2, d\Omega)$ spanned by $Y_{\ell,-\ell}, \ldots, Y_{\ell,\ell}$, to separate over the basis of spherical harmonics. We make the unitary transformation $U : L^2(\mathbb{R}^+, r^2 dr) \rightarrow L^2(\mathbb{R}^+, dr)$ given by $(U \chi)(r) = r \chi(r)$ to obtain the radial Hamiltonians for each angular momentum sector

$$
h_{\ell} = -\frac{d^2}{dr^2} + \frac{\ell(\ell + 1)}{r^2} + \frac{\gamma}{r} \tag{2.7}
$$

which we define on $C^\infty_0(0, \infty) \subset L^2(\mathbb{R}^+, dr)$. (Studying the $h_{\ell}$ on this domain is actually equivalent to studying $H_{\text{ideal}}$ on $\mathcal{D}$, the set of finite linear combinations of terms of form $f(r)Y_{\ell,m}(\theta, \varphi)$ where $f(r) \in C^\infty_0(0, \infty)$. However, this can be seen to yield the same deficiency subspaces and self-adjoint extensions as are obtained with $\mathcal{D} = C^\infty_0(\mathbb{R}^3 \setminus \{0\})$.)

Solving $h_{\ell}^* u_{\ell}^\pm = \pm i u_{\ell}^\pm$ as an ODE yields, as solutions square integrable at infinity

$$
u_{\ell}^\pm = \mathcal{W}_{-i\gamma/2(\pm i)^{1/2},\ell+1/2}(-2i(\pm i)^{1/2}r) \tag{2.8}
$$

where $\mathcal{W}_{\kappa,\mu}(z)$ is a Whittaker function [18]. For $\ell \geq 1$, these functions are not square integrable at the origin and so the $h_{\ell}$ are essentially self-adjoint. In the case $\ell = 0$, however, the functions $u_0^\pm$ are square integrable, so $h_0$ has deficiency indices $(1,1)$ and a 1-parameter family of self-adjoint extensions labelled by $U(1)$, or
equivalently (under an obvious correspondence) by the extended real line \( \mathbb{R} \cup \{ \infty \} \).

These may be denoted

\[ h^L_0 = \{ u \in L^2(\mathbb{R}^+) \mid u, u' \in AC_{\text{loc}}(\mathbb{R}^+); \ u'' + \gamma r^{-1}u \in L^2(\mathbb{R}^+), \ [L^{-1} + \gamma(\Psi(1) + \Psi(2))]u_0 + u_1 = 0 \} \tag{2.9} \]

where \( u_0 = \lim_{r \to 0^+} u(r) \), \( u_1 = \lim_{r \to 0^+} r^{-1}(u(r) - u_0(1 + \gamma r \log(|\gamma| r))) \). Here \( AC_{\text{loc}}(\mathbb{R}^+) \) denotes the set of locally absolutely continuous functions on the positive half-line, and \( \Psi(z) \equiv d/dz \log \Gamma(z) \) is the di-gamma function. \( u_1 \) can be regarded as a ‘Coulomb modified’ first derivative (from the right) of \( u(r) \) at \( r = 0 \). Note that the usual Hamiltonian, with regular boundary conditions, arises from the choice \( L = 0 \).

The spectrum of \( h^L_0 \) in the case \( \gamma < 0 \) was first discussed by Rellich [6] (see [5] for the \( \gamma > 0 \) case). For each value of \( L \), there are infinitely many non-degenerate negative eigenvalues of \( h^L_0 \). The eigenfunctions are precisely those solutions \( v(r) \) to

\[ \left( -\frac{d^2}{dr^2} + \frac{\gamma}{r} \right) v = -\kappa^2 v \tag{2.10} \]

which are square integrable and lie in the domain (2.9) above. The first requirement entails that \( v(r) \) is given (up to normalisation) in terms of the Whittaker function by

\[ v(r) = W_{0|\gamma|/2\kappa}^{\frac{\gamma}{2}}(2\kappa r). \tag{2.11} \]

Defining

\[ v_0 = \lim_{r \to 0^+} v(r), \quad v_1 = \lim_{r \to 0^+} r^{-1}(v(r) - v_0(1 + \gamma r \log(|\gamma| r))) \],

we find

\[ \frac{v_1}{v_0} = \gamma \left[ \log \frac{2\kappa}{|\gamma|} - \Psi(1) - \Psi(2) + \Psi(1 + \gamma/2\kappa) - \kappa/\gamma \right] \tag{2.12} \]

and hence (by our second requirement) that eigenvalues occur for \( E = -\kappa^2 \) satisfying

\[ \frac{a_o}{2L} = -\frac{1}{\gamma L} = G \left( \frac{\gamma}{2(-E)^{1/2}} \right) \]

where the function \( G \) is defined by

\[ G(z) = \Psi(1 + z) - \log |z| - 1/(2z). \tag{2.14} \]

\( G(z) \) is everywhere increasing in \( z \in \mathbb{R} \) except at its poles, located at \( z = -n \) for \( n = 0, 1, 2, \ldots \), and so \( G(z) \) increases from \( -\infty \) to \( \infty \) between each consecutive pair of poles (see Fig. 2.1). There is therefore precisely one zero \( z_n \) of \( G(z) \) between each consecutive pair of negative integers \( z_n \in (-n, -n + 1) \) for \( n = 1, 2, \ldots \) and precisely one solution of (2.13) for \( \gamma/(2(-E)^{1/2}) \) in the interval \( (z_n + 1, z_n) \) for each \( n = 1, 2, \ldots \). We label the corresponding energy by \( E_n \). For \( L > 0 \), there is

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\(^1\)Our parametrisation differs from that in [5]. This will be convenient later.
also an eigenvalue $E_0$, with $\gamma/(2(-E_0)^{1/2} \in (z_1, 0)$. In addition, the special case $L = 0$ – which corresponds by (2.9) to the case of regular boundary conditions at the origin – gives rise to the usual Bohr levels

$$E_n = -\frac{\gamma^2}{4n^2} \quad n = 1, 2, \ldots$$

(2.15)

However, we see that by changing $L$, we can radically alter the eigenvalues. The eigenvalues $E_n$ for $n \geq 1$ are subject to maximum fractional changes of order $1/n$, and for all $L \geq 0$, there is an additional eigenvalue $E_0$ lying well below the usual Bohr levels. Thus the ground state and first few excited energy levels can be quite sensitive to the value of $L$. However, if $|L| \ll a_0$, we can see (comparing with Fig. 2.1) that the energy levels are little changed from the Bohr levels. Indeed, in such cases, because $\Psi(1 + \xi) = -\frac{1}{(\xi + n)^{-1} + O(1)}$ as $\xi \to -n - 1$ for all $n = 1, 2, \ldots$, we may write the second equality in (2.13) in the approximate form

$$-\frac{1}{\gamma L} \approx -\frac{1}{\gamma/2(-E)^{1/2} + n}$$

(2.16)

obtaining the approximate solutions

$$E_n = -\frac{\gamma^2}{4(n - \gamma L)^2} = -\frac{\gamma^2}{4(n - 2L/a_0)^2}.$$  

(2.17)

Thus $2L/a_0$ plays the rôle of the Rydberg correction (or quantum defect) of atomic physics [13]. In addition for $0 < L \ll a_0$, because $G(\xi) = -(2\xi)^{-1} + O(\log |\xi|)$ as $\xi \to 0$, we have an energy level $E_0$ lying well below the Bohr spectrum

$$E_0 \approx -\frac{1}{L^2}.$$  

(2.18)

The presence of such a deeply bound state is initially puzzling, and we shall return to this in Section 4.

As noted above, for $\ell \geq 1$, the operators $h_{\ell}$ are essentially self-adjoint on the domain $C_0^\infty(0, \infty)$ and so there is a unique self-adjoint extension $\tilde{h}_\ell$ whose eigenvalues are simply the familiar Bohr levels:

$$E_{\ell,n} = -\frac{\gamma^2}{4(n + \ell)^2} \quad n = 1, 2, \ldots$$

(2.19)

By analogy, we will abuse notation and write $\tilde{h}_0$ to denote $h_{\ell}$. We may therefore assemble the radial Hamiltonians to give the full Hamiltonian $H^L$ (recalling the decomposition (2.6)) defined by

$$H^L = U^*h_0^L U \otimes \mathbb{I} \oplus \bigoplus_{\ell=1}^\infty U^*\tilde{h}_\ell U \otimes \mathbb{I}$$

(2.20)
which acts on the $S$-wave as $h_0^L$ and as $\bar{h}_\ell$ on the $\ell$'th sector for $\ell \geq 1$. The spectral properties of $H^L$ are immediately given by the discussion above.

The case $H^0$ corresponds to the usual choice of idealisation with regular boundary conditions. This operator is the closure of $H_{\text{ideal}}$ on $C_0^\infty(\mathbb{R}^3)$ and would therefore result if we treated the idealised problem in the same way as true problems by assuming finiteness of the wavefunction as an axiom. We emphasise that Theorem 2.1 shows that it would be inconsistent to do this.

To summarise, there is a 1-parameter family of idealised Hamiltonians arising as self-adjoint strong resolvent limits of sequences of true problem Hamiltonians whose nuclear radii shrink to zero. The idealisations $H^L$ are the self-adjoint extensions of $-\triangle + \gamma/r$ on $C_0^\infty(\mathbb{R}^3\setminus\{0\})$ which are labelled by a single real parameter $L \in \mathbb{R} \cup \{\infty\}$ (later, we will identify $L$ as a Coulomb modified scattering length). The idealisations differ from the usual Hamiltonian $H^0$ only in the $S$-wave, in which the low-lying energy levels can exhibit significant fractional changes from the Bohr levels, depending on the value of $L$. In addition, for all non-zero values of $L$, there is an additional bound state lying below the usual Bohr spectrum. We will discuss this bound state later in Section 4.

### 3 The Regular Boundary Condition

We now turn to our rigorous justification of the regular boundary condition. Central to this is the mild physical requirement that the correction potential $V$ is positive and has nuclear radius $a \ll a_0$. Under these assumptions, we will see that the spectrum of the true problem is well approximated by the Bohr levels. In the following, for any self-adjoint operator $H$ bounded from below, $\mu_n(H)$ denotes (when it exists), the $n$'th discrete eigenvalue of $H$, counting with multiplicity and in increasing order.

Given positive $V \in \mathcal{V}$, we define the $S$-wave radial true Hamiltonian $h_{0,\text{true}} = \bar{h}_0 + V$. Suppose $V$ has nuclear radius $a$. Because $V$ is positive, the $n$'th eigenvalue $\mu_n(h_{0,\text{true}})$ is bounded below by the $n$'th Bohr level $\mu_n(\bar{h}_0)$. Moreover, it is resonable to suppose that an upper bound should be provided by the $n$'th eigenvalue of $h'_0$, the Hamiltonian describing an impenetrable nucleus of radius $a$ which corresponds to the heuristic potential

$$V(r) = \begin{cases} \infty & r < a \\ 0 & r \geq a. \end{cases} \quad (3.1)$$

In fact, this turns out to be the case. We define $h'_0$ defined on $L^2([a, \infty), dr)$ by

$$h'_0 = \left(-\frac{d^2}{dr^2} + \frac{\gamma}{r}\right) \upharpoonright \mathcal{D}' \quad (3.2)$$

where

$$\mathcal{D}' = \{ \psi \mid (r-a)^{-1}\psi \in C_0^\infty([a, \infty)) \} \subset L^2([a, \infty), dr). \quad (3.3)$$
The domain $D'$ is chosen to ensure that all eigenfunctions vanish at the radius $r = a$. In the Appendix, we prove that this Hamiltonian has precisely one eigenvalue between each consecutive pair of Bohr levels and no other eigenvalues. (In addition there is essential spectrum $[0, \infty)$.) Note that this Hamiltonian is defined on a different Hilbert space from $\mathcal{h}_{0, \text{true}}$. In Section 6, we prove

**Theorem 3.1** Let $h_{0, \text{true}} = \bar{h}_0 + V$ for some positive $V \in \mathcal{V}$ with nuclear radius $a > 0$ and define $h'_0$ by (3.2) for this choice of $a$. Then $\bar{h}_0$, $h_{0, \text{true}}$ and $h'_0$ are bounded from below and possess infinitely many eigenvalues satisfying

$$\mu_n(\bar{h}_0) \leq \mu_n(h_{0, \text{true}}) \leq \mu_n(h'_0)$$

for each $n = 1, 2, \ldots$.

In the case $a \ll a_0$, the energy levels of $h'_0$ are estimated in the Appendix as

$$\mu_n(h'_0) \approx -\frac{\gamma^2}{4(n + 2a/a_0)^2}$$

Hence (3.4) may be re-written

$$-\frac{\gamma^2}{4n^2} \leq \mu_n(h_{0, \text{true}}) \leq -\frac{\gamma^2}{4n^2} \left[1 - \frac{4a}{na_0}\right]$$

and so, using $a/a_0 \sim 10^{-5}$, the maximum fractional error for the physical hydrogen atom is of order $10^{-5}$.

Hence we see that the energy levels of the true problem are close to the Bohr levels, provided the correction to the Coulomb potential is positive and that the nuclear radius is smaller than the Bohr radius. Note that the bound (3.6) is considerably weaker than the usual perturbative estimate of the energy shift due to the finite size and structure of the nucleus [14], which assumes the nucleus is a smoothed out region of positive charge and works to first order in perturbation theory, obtaining energy shifts of order $(a/a_0)^2$. However, the result above is non-perturbative and covers a much greater range of nuclear models, including many for which first order perturbation theory would break down. In the next section, we will describe how a general true problem can be modelled by the idealised problem with potentially irregular boundary conditions, and how the usual perturbative result may be derived within this formalism.

As a second justification of the regular boundary condition, we consider sequences of Hamiltonians with positively corrected Coulomb potentials. Recall that $\Sigma$ denotes the class of sequences of true problem Hamiltonians $H_n = -\Delta + \gamma/r + V_n(r)$ whose nuclear radii tend to zero. Our space of general regularisation schemes is therefore $\Sigma$. In general, Theorem 2.1 – which defines our notion of idealisation – shows that class of the possible self-adjoint limits of such sequences in the strong resolvent sense is precisely the class of self-adjoint extensions of $H_{\text{ideal}}$ on $C_0^\infty(\mathbb{R}^3 \setminus \{0\})$. Thus, in general, the limit (when it exists) is not
the self-adjoint extension with regular boundary conditions. However, restricting to the subclass \( \Sigma^+ \subset \Sigma \) of sequences \( H_n = -\Delta + \gamma/r + V_n(r) \) in which the potentials \( V_n \) are positive, it turns out that all such sequences converge in the strong resolvent sense.

**Theorem 3.2** *All sequences in \( \Sigma^+ \) converge in the strong resolvent sense to \( H^0 \), the self-adjoint extension of \( H_{\text{ideal}} \) with regular boundary conditions.*

Thus any regularisation scheme in \( \Sigma^+ \) selects the regular boundary condition, providing our second justification.

### 4 Scattering Length Formalism

In this section, we consider how a general true problem may be approximated by an appropriate choice of idealised problem. The starting point for our discussion is the low energy expansion of Coulomb modified scattering theory developed by Lambert [12]. This will enable us to examine the behaviour of both true problems and idealisations at energies small in comparison with the nuclear scale, i.e. \( E \ll a^{-2} \). This regime covers the atomic spectrum, whose characteristic scale is the Bohr radius, 5 orders of magnitude larger than the atomic radius for the physical hydrogen atom. The ‘best fit’ boundary condition can then be found by matching the low energy behaviour of the idealisation to the true problem. The procedure below is the direct generalisation of the treatment of the non-Coulombic case in [3].

In the \( S \)-wave, we therefore examine the regular solution \( u(r) \) to

\[
\left\{ -\frac{d^2}{dr^2} + \frac{\gamma}{r} + V(r) \right\} u = k^2 u
\]

where \( V(r) \) obeys \( r^2 V(r) \to 0 \) as \( r \to 0 \) and is compactly supported within some radius \( a \) of the origin. These conditions allow all potentials in our class \( \mathcal{V} \).

The Coulomb modified phase shift \( \delta_0(k) \) is defined by writing the asymptotic form of the regular solution to (4.1) as

\[
u(r) \sim \sin(kr - (\gamma/(2k)) \log 2kr + \sigma_0(k) + \delta_0(k))
\]

where \( \sigma_0(k) \) is given by

\[
e^{2i\sigma_0(k)} = \frac{\Gamma(1 + i\gamma/2k)}{\Gamma(1 - i\gamma/2k)}.
\]

Defining

\[
Z^\ast(k) = \pi \gamma (e^{(2\pi k)/\gamma} - 1)^{-1} \cot \delta_0(k) + \frac{\gamma}{2} \left[ \Psi \left( \frac{i\gamma}{2k} \right) + \Psi \left( -\frac{i\gamma}{2k} \right) \right] - \gamma \log \left| \frac{\gamma}{2k} \right|,
\]

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we have the (Coulomb modified) low energy expansion (see e.g. [12])

$$Z^c(k) = -\frac{1}{L} + \frac{1}{2}r_0k^2 + O(k^4)$$

(4.5)

where $L$ and $r_0$ are the Coulomb modified scattering length and effective range respectively. This is the analogue of the familiar low energy expansion of scattering theory for short range forces [11].

It can be shown [5] that the scattering theory of the idealised Hamiltonian $H^L$ is described by the $S$-wave low energy expansion

$$Z^c(k) = -\frac{1}{L}.$$  

(4.6)

(For angular momenta $\ell \geq 1$, there is, of course, no scattering.) Thus the operator $H^L$ has a low energy expansion which is exact at lowest order. We are also able to interpret the parameter $L$ as the (Coulomb modified) scattering length of $H^L$. It is therefore clear from this and equation (4.5) that scattering theory of $H^L$ describes the leading order scattering theory of any true problem with scattering length $L$ at low energies. Moreover, because the low energy expansion may be analytically continued to discuss bound states, $H^L$ should also well-approximate the bound states of any true problem with scattering length $L$ at sufficiently low energies. It is therefore possible to select the ‘best fit’ idealisation to a given true problem simply by matching the scattering lengths.

In order to compute the scattering length of a given true problem, it suffices to consider the regular solution $u(r)$ to (4.1) at zero energy, i.e. $k^2 = 0$. Lambert showed [12] that the scattering length is then given by

$$L = \frac{\phi(a)}{\theta(a)} - \frac{1}{\theta(a)^2} \left. \left( \frac{u'(r)}{u(r)} - \frac{\theta'(r)}{\theta(r)} \right) \right|_{r=a}^{-1}.$$  

(4.7)

Because this formula allows us to select the best fit idealisation to the true problem, we refer to it as the fitting formula. Here,

$$\phi(r) = \left( \frac{r}{|\gamma|} \right)^{1/2} J_1(2(|\gamma| r)^{1/2})$$  

(4.8)

and

$$\theta(r) = -\pi (|\gamma| r)^{1/2} N_1(2(|\gamma| r)^{1/2})$$  

(4.9)

(where $J_1(z)$ and $N_1(z)$ are the Bessel and Neumann functions of order 1 [18]) are the regular and irregular solutions to (4.1) in the special case $V \equiv 0$, $k = 0$. Note that $\phi$ and $\theta$ have Wronskian $\phi'\theta - \theta'\phi \equiv 1$. The effective range may also be determined using $u$, $\phi$ and $\theta$ [12].

It is, of course important to know the range of energies over which this approximation holds good. In [3], this is referred to as the question of believability. As
a simple necessary condition – derived by requiring that the second term in (4.5) be small compared with the first – we say that the idealisation is believable at energy $E$ only if

$$|E| \ll \frac{1}{|L_{ro}|}$$

(4.10)

where $L$ and $r_o$ are the scattering length and effective range of the true problem.

As we noted in Section 2, for $L \gtrsim a_0$, the $S$-wave energy levels exhibit significant fractional changes from the Bohr levels. From this it is to be expected that the low-lying energy levels of an atom differ markedly from the Bohr levels if the nucleus has scattering length of the order of, or greater than, the Bohr radius. It is therefore important to know whether the scattering length can take such values. In fact a simple argument shows that for any $L \in \mathbb{R} \cup \{\infty\}$ there exist potentials $V(r)$ of arbitrarily small support with scattering length $L$: let $r \mapsto \psi(|r|)$ be any smooth spherically symmetric function on $\mathbb{R}^3$ with $\psi(|r|)$ bounded away from zero for $r < a$ and $\psi(r) = r^{-1}(\phi(r) - L\theta(r))$ for $r \geq a$. Then the potential $V(r)$ defined by

$$V(r) = \psi^{-1}\Delta\psi - \frac{\gamma}{r}$$

(4.11)

is supported within $r < a$ and the effective potential $\gamma/r + V(r)$ is smooth on $\mathbb{R}^3$. Moreover, by (4.11) and the first property, $V(r)$ has scattering length $L$. We have therefore proved

**Theorem 4.1** For any $L \in \mathbb{R} \cup \{\infty\}$, and any $a > 0$, there exists a potential $V \in \mathcal{V}$ with nuclear radius less than $a$ and with (Coulomb modified) scattering length $L$.

Thus there exist true problems with ‘nuclei’ of arbitrarily small radius whose energy levels at sufficiently small energy (i.e. for large enough principal quantum number) are well-approximated by the energy levels of $H^L$, for any $L \in \mathbb{R} \cup \{\infty\}$. One can use ‘believability’ to determine the range of energies for which this approximation is valid. Provided the effective range (and all higher parameters in the low energy expansion) is small, the approximation could include the energy levels of low principal quantum number. Concrete examples are given in [2].

We now restrict to the case of positive corrections $V \in \mathcal{V}$ to the Coulomb potential. We take the nuclear radius to be $a$ and define $u(r)$ and $\phi(r)$ as above, noting that they satisfy

$$\phi(r)u''(r) - u(r)\phi''(r) = V(r)\phi(r)u(r).$$

(4.12)

The first zero of $\phi(r)$ away from the origin occurs at approximately $1.8a_0$, and that of $\theta(r)$ at $a_1 \sim 0.6a_0$. Restricting to the case $a < a_1$ (which therefore includes the physical case $a \sim 10^{-5}a_0$), we have $\phi \geq 0$ on $(0, a)$ and we may write

$$\phi(r)^2 \frac{d}{dr} \left( \frac{u(r)}{\phi(r)} \right) = \phi(r)u'(r) - u(r)\phi'(r) = \int_0^r V(r')\phi(r')u(r')dr'.$$

(4.13)
Because $r^2 V(r) \to 0$ as $r \to 0$ and $u, \phi$ both obey regular boundary conditions at the origin, we may divide through by $\phi^2$ to yield an integrable function, leading to the following integral equation for $u(r)$

$$u(r) = \phi(r) + \phi(r) \int_0^r dr'(\phi'(r'))^{-2} \int_0^{r'} dr'' V(r'') \phi(r'') u(r'').$$  \hfill (4.14)

Since $\phi(r) > 0$ on $(0, a)$, we conclude that $u(r)$ is also strictly positive on this interval, for by the second equality in (4.13), $u$ could vanish only if $u'$ is positive. Therefore, because $u(r)$ is initially positive, it must remain so on this interval ($V(r)$ is sufficiently regular that $u(r)$ remains bounded on $(0, a)$). Hence we obtain the relation

$$\frac{u'(r)}{u(r)} - \frac{\phi'(r)}{\phi(r)} = \frac{\int_0^r V(r') \phi(r') u(r') dr'}{\phi(r) u(r)} > 0.$$  \hfill (4.15)

Inserting this in the fitting formula (4.17) and using the fact that $\phi$ and $\theta$ have unit Wronskian and are positive on $(0, a)$, we find that the Coulomb modified scattering length for such a potential satisfies

$$0 < L < \frac{\phi(a)}{\theta(a)}. \hfill (4.16)$$

The trivial case $V(r) \equiv 0$ yields vanishing scattering length. We have thus proved

**Theorem 4.2** Let $V \in V$ be positive and supported within $[0, a)$, where $a < a_1$. Then the scattering length of $V$ is bounded by

$$0 \leq L < \frac{\phi(a)}{\theta(a)} = L_{\text{max}}.$$  \hfill (4.17)

Furthermore, if $a < a_0/8$, then a reasonable approximation to the upper bound is provided by $a$, the nuclear radius, so we can write

$$0 \leq L \lesssim a.$$  \hfill (4.18)

We can substitute this inequality into the approximate expression (2.17) in order to re-derive equation (3.6) as a useful consistency check (although the derivation in this section truncates the low energy expansion at first order and is therefore less rigorous than our previous derivation). In fact, we show in the Appendix that the $n+1$'st eigenvalue of $h_0^{L_{\text{max}}}$ provides an upper bound on the $n$'th eigenvalue of $h_0$ and hence (by Theorem 3.1) on the $n$'th eigenvalue of $h_0$, true for a positive correction to the Coulomb potential. Note that, for $0 < L \lesssim a$, the idealisation $H^L$ also exhibits a energy level $E_0(L) \sim -L^{-2}$ lying well below the Bohr spectrum, as we saw in Section 2. However, we can use believability to
show that this is not a believable feature of the true system, at least in the case where the effective range is of the order of the nuclear radius, when the range of believability is

\[ |E| \ll \frac{1}{a^2} < \frac{1}{L^2} \quad (4.19) \]

so the bound state \( E_0 \approx -1/L^2 \) falls outside this range. The presence of this bound state is therefore a result of the idealisation process which does not in this case correspond to any feature of the true problem. This is reassuring, because it is, of course, impossible for a positive correction to the Coulomb potential to introduce a new energy level below the Bohr levels. This provides a simple example of the manner in which the components of the scattering length formalism and believability work together.

5 Higher Angular Momenta

The discussion in Sections 3 and 4 demonstrated two features of the true problem in the \( S \)-wave. Theorem 3.1 showed that for positive corrections to the Coulomb field of small nuclear radii, the true spectrum is well approximated by the Bohr levels. On the other hand, Theorem 4.1 showed that there exist true problems with arbitrarily small nuclear radius whose spectra depart significantly from the Bohr levels. In this section, we examine the true problem for higher angular momenta and discover that not only are the Bohr levels stable against positive perturbations, they are also remarkably stable against general perturbations in a manner we will specify below. This can be traced directly to the fact that \( C^\infty_0(0, \infty) \) is a core for the radial Hamiltonians \( \bar{h}_\ell \), in contrast to the \( \ell = 0 \) case, where the deficiency indices are \( (1,1) \).

We firstly examine the case \( V(r) \geq 0 \). Here, we have the analogue of Theorem 3.1: for \( a > 0 \) we define \( h'_\ell \) on \( L^2([a, \infty), dr) \) by

\[
h'_\ell = \left(-\frac{d^2}{dr^2} + \frac{\ell(\ell + 1)}{r^2} + \frac{\gamma}{r}\right) \upharpoonright D'
\]

where

\[
D' = \{ \psi \mid (r - a)^{-1}\psi \in C^\infty_0([0, \infty)) \} \subset L^2([a, \infty), dr).
\]

We have

**Theorem 5.1** For any \( \ell \), let \( h_{\ell,\text{true}} = \bar{h}_\ell + V \) for some positive \( V \in \mathcal{V} \) with nuclear radius \( a > 0 \). Define \( h'_\ell \) by (5.1) for this choice of \( a \). Then \( \bar{h}_\ell, h_{\ell,\text{true}} \) and \( h'_\ell \) are bounded from below and possess infinitely many eigenvalues satisfying

\[
\mu_n(\bar{h}_\ell) \leq \mu_n(h_{\ell,\text{true}}) \leq \mu_n(h'_\ell)
\]

for each \( n = 1, 2, \ldots \).
In the Appendix, we estimate the energy levels of $h'_\ell$ as

$$\mu_n(h'_\ell) = -\frac{\gamma^2}{4(n + \ell + \xi_n)^2}$$

for $n = 1, 2, \ldots$, where

$$\xi_n \approx \frac{(n + 2\ell)!}{(2\ell + 1)!(2\ell)!}(\frac{2}{n + \ell})^{2\ell+1}\left(\frac{a}{a_0}\right)^{2\ell+1}.$$  \hfill (5.5)

Thus for positive corrections of small nuclear radius, the spectrum is well approximated by the Bohr levels.

So far we have only considered spherically symmetric potentials $V$. We state (but do not prove) an easy generalisation of Theorems 3.1 and 5.1 to the general case.

**Theorem 5.2** Let $H_{\text{true}} = H^0 + V(r)$ where $H^0$ is the idealisation with regular boundary conditions and $V$ is positive and compactly supported within some radius $a$ of the origin and such that $r \mapsto \gamma |r|^{-1} + V(r)$ is smooth on $\mathbb{R}^3$. Defining the $h'_\ell$ for this choice of $a$, let

$$H' = \bigoplus_{\ell=0}^\infty U^* h'_\ell U.$$  \hfill (5.6)

Then $H^0$, $H_{\text{true}}$ and $H'$ are all bounded from below and possess infinitely many eigenvalues satisfying

$$\mu_n(H^0) \leq \mu_n(H_{\text{true}}) \leq \mu_n(H')$$  \hfill (5.7)

for each $n = 1, 2, \ldots$.

Turning to case of general spherically symmetric potentials $V \in \mathcal{V}$, the situation is as follows: the Bohr levels are preserved to arbitrary accuracy by all true problems of sufficiently small nuclear radius. To understand this precisely, consider a *gedanken* experiment in which one examines true problems in the laboratory, using a spectrometer which resolves energies down to tolerance $\delta E$. Clearly, only finitely many spectral lines would be observed. In the $S$-wave, one can find true problems of arbitrarily small nuclear radius for which the spectral lines depart significantly from those corresponding to the Bohr levels. In the sectors $\ell \geq 1$, however, all true problems of sufficiently small support would apparently yield the spectral lines of the Bohr levels (up to the tolerance of the spectrometer) with the additional possibility of extra spectral lines. The important point is that the structure of the Bohr levels is substantially preserved, in contrast to the $\ell = 0$ case.

These statements follow from the following result, which we prove in Section 6.
Theorem 5.3 Suppose \( \ell \geq 1 \) and let \( \lambda \) be an element of the spectrum of \( \bar{h}_\ell \). Given \( \epsilon > 0 \), there exists a radius \( a_\ell(\lambda, \epsilon) > 0 \) such that, for any potential \( V \in \mathcal{V} \) supported within \( [0, a_\ell(\lambda, \epsilon)) \)

\[
\text{dist}(\lambda, \sigma(h_{\ell,\text{true}})) < \epsilon
\]

where \( h_{\ell,\text{true}} = \bar{h}_\ell + V \) and \( \text{dist}(x, Y) = \inf_{y \in Y} \| x - y \| \).

This result is a direct consequence of the fact that \( C_0^\infty(0, \infty) \) is a core for \( \bar{h}_\ell \).

Our statement above is an immediate corollary of Theorem 5.3:

Corollary 5.4 Suppose \( \ell \geq 1 \). Given \( \epsilon > 0 \), there exists \( a_\ell(\epsilon) > 0 \) such that, for all \( V \in \mathcal{V} \) supported within \( [0, a_\ell(\epsilon)) \),

\[
\text{dist}(\lambda, \sigma(h_{\ell,\text{true}})) < \epsilon
\]

for all \( \lambda \in \sigma(\bar{h}_\ell) \), where \( h_{\ell,\text{true}} = \bar{h}_\ell + V \).

Proof: Given \( \epsilon > 0 \), equation (5.9) is non-trivial only for finitely many eigenvalues \( \lambda \) of \( \bar{h}_\ell \). \( a_\ell(\epsilon) \) may then be taken to be the minimum value of the \( a_\ell(\lambda, \epsilon) \) furnished by Theorem 5.3 over these \( \lambda \). \( \square \)

An important feature of the above results is that they do not preclude the existence of extra energy levels, in addition to those close to Bohr levels. (This arises because our proof in Section 6 makes use of strong resolvent convergence.) Indeed, one may see that such levels can occur by considering a potential well within the nucleus which is gradually deepened gradually pulling bound state well below the Bohr spectrum. The remarkable feature of these results is that even during such a process, the Bohr levels remain well approximated (up to given accuracy) by eigenvalues of the true problem in angular momentum sectors \( \ell \geq 1 \).

The principal limitation of Theorem 5.3 and Corollary 5.4 is that they are pure existence results; we have gained no information on the magnitude of \( a_\ell(\lambda, \epsilon) \). Numerical investigations, however, suggest that, for example, all true problems with nuclear radius \( a \sim 10^{-5} \times a_0 \) have \( P \)-wave energy levels within 2\% of each of the lowest five \( P \)-wave Bohr levels.

6 Rigorous Proofs

In this section, we provide the proofs of the theorems stated above. We begin by developing a sufficient condition for a sequence \( A_n \) of self-adjoint operators to converge to a self-adjoint limit \( A \). Our condition is only slightly weaker than that given by Theorem VIII.26 in [15] (which we will also use) and the proof is similar. In the sequel we will often use the concepts of the graph of an operator and also the strong graph limit of a sequence of operators:
Definition 6.1 The graph $\Gamma(A)$ of an operator $A$ on a Hilbert space $\mathcal{H}$ is the set of pairs $\langle \psi, A\psi \rangle \in \mathcal{H} \times \mathcal{H}$ where $\psi$ runs through the domain of $A$. If $\{A_n\}$ is a sequence of operators on $\mathcal{H}$, the strong graph limit of the $A_n$ is the set of pairs $\langle \phi, \psi \rangle \in \mathcal{H} \times \mathcal{H}$ for which there exists a sequence $\phi_n$ satisfying $\phi_n \in D(A_n)$, $\phi_n \to \phi$ and $A_n\phi_n \to \psi$.

We now give our sufficient condition for strong resolvent convergence.

Proposition 6.2 Let $\{A_n\}$ and $A$ be self-adjoint on $\mathcal{H}$ and let $\mathcal{D}$ be a core for $A$. If the graph of $A$ restricted to $\mathcal{D}$ is contained in the strong graph limit of the $A_n$, then $A_n \to A$ in the strong resolvent sense.

Proof: Take $\phi \in \mathcal{D}$. Then there exists a sequence $\{\phi_n\}$, $\phi_n \in D(A_n)$ with $\phi_n \to \phi$ and $A_n\phi_n \to A\phi$. For any $z \in \mathbb{C}\setminus \mathbb{R}$, we have

\[
\left[ (A_n + z)^{-1} - (A + z)^{-1} \right] (A + z)^{-1} = (A_n + z)^{-1} \left[ (A + z)\phi - (A_n + z)\phi_n \right] + \phi_n - \phi \to 0
\]

as $n \to \infty$, because the $(A_n + z)^{-1}$ are a uniformly bounded family of operators. Thus we have

\[
(A_n + z)^{-1}\psi \to (A + z)^{-1}\psi
\]

for all $\psi \in \text{Ran}((A + z) \upharpoonright \mathcal{D})$, which is dense in $\mathcal{H}$ because $\mathcal{D}$ is a core for $A$. The result therefore extends to all $\psi \in \mathcal{H}$ because the $(A_n + z)^{-1}$ and $(A + z)^{-1}$ are uniformly bounded. \(\square\)

We will also need Theorem VIII.26 of [15]:

Proposition 6.3 Let $\{A_n\}$ and $A$ be self-adjoint on $\mathcal{H}$. $A_n \to A$ in the strong resolvent sense if and only if the graph of $A$ is the strong graph limit of the $A_n$.

We study two classes of sequences of true problem Hamiltonians whose nuclear radii shrink to zero: $\Sigma$ and $\Sigma^+$. A particularly useful feature of such sequences is that, for any smooth wavefunction $\psi$ compactly supported away from the origin, $H_n\psi = (\Delta + \gamma/r)\psi$ as $n \to \infty$, because the support of the correction to the Coulomb field eventually lies closer to the origin than the support of $\psi$. In terms of graphs, this shows that the graph of $H_{\text{ideal}} = -\Delta + \gamma/r$ on $C^\infty_0(\mathbb{R}^3 \setminus \{0\})$ is contained in the strong graph limit of any sequence in $\Sigma$.

In the results below, it will be useful to have available explicit cores $\mathcal{D}^L$ for the self-adjoint extensions $H^L$ of $H_{\text{ideal}}$. To this end, we define the mollified zero energy wavefunction $\chi^L$ of $H^L$ by

\[
\chi^L(r) = g(r) r^{-1} (\phi(r) - L\theta(r))
\]

where $g(r)$ is a smooth mollifier satisfying $g(r) = 1$ for $r < a_0$ and vanishing for $r > 2a_0$. Clearly $\chi^L \in L^2(\mathbb{R}^3, d^3r)$. We now define

\[
\mathcal{D}^L = C^\infty_0(\mathbb{R}^3 \setminus \{0\}) + \{ \lambda \chi^L \mid \lambda \in \mathbb{C} \}
\]

and show that it is a core for $H^L$. 

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Lemma 6.4 $D^L$ is a core for $H^L$.

Proof: $H^L \upharpoonright D^L$ is clearly symmetric and extends $H_{\text{ideal}}$, so $H_{\text{ideal}}^*$ extends $(H^L \upharpoonright D^L)^*$. Therefore the deficiency subspaces of $H^L \upharpoonright D^L$ are contained within those of $H_{\text{ideal}}$. However, a simple integration by parts argument shows that neither of the functions $\psi^\pm_0 = r^{-1}u^\pm_0$ are in the domain of $(H^L \upharpoonright D^L)^*$, where $u^\pm_0$ are defined in (2.8). Since $\psi^\pm_0$ span the two 1-dimensional deficiency subspaces of $H_{\text{ideal}}$, it is clear that the deficiency indices of $H^L$ on $D^L$ are $\langle 0, 0 \rangle$, so that $D^L$ is a core for $H^L$. □

We begin with Theorem 2.1 which demonstrates the connection between the limit points of sequences in $\Sigma$ and the self-adjoint extensions of $H_{\text{ideal}}$.

Theorem 2.1 Let $H_{\text{ideal}} = -\Delta + \gamma/r$ on $C_0^\infty(\mathbb{R}^3 \setminus \{0\})$. (a) Let $\{H_n\} \in \Sigma$. If $\{H_n\}$ has a self-adjoint limit in the strong resolvent sense, then $H$ is a self-adjoint extension of $H_{\text{ideal}}$. (b) Furthermore, all self-adjoint extensions of $H_{\text{ideal}}$ arise as the strong resolvent limits of sequences in $\Sigma$.

Proof: (a) Suppose that $\{H_n\}$ has a self-adjoint limit. Then by Proposition 6.3, the strong graph limit of the $H_n$ is equal to the graph of $H$. Furthermore, our observation above shows that the graph of $H$ necessarily contains the graph of $H_{\text{ideal}}$. Hence $H$ is a self-adjoint extension of $H_{\text{ideal}}$.

(b) Now suppose that $H^L$ is the self-adjoint extension of $H_{\text{ideal}}$ with scattering length $L$. By Lemma 6.4, we know that $D^L$ is a core for $H^L$. Proposition 6.2 shows us that it is enough to construct a sequence $\{H_n\} \in \Sigma$ whose strong graph limit contains the graph of $H^L$ restricted to $D^L$. In fact, as we know that the strong graph limit of any sequence in $\Sigma$ contains the graph of $H_{\text{ideal}}$, it is enough to construct such a sequence whose strong graph limit contains the pair $\langle \chi^L, H^L\chi^L \rangle$. In order to do this, we employ similar arguments to those used in the proof of Theorem 1.1 to construct a sequence of potentials of decreasing support all of which have scattering length $L$. Specifically, let the $\chi_n(r)$ be smooth spherically symmetric compactly supported functions on $\mathbb{R}^3$ satisfying

1. $\chi_n(r) = \chi^L(r)$ for $r > a_0/n$
2. $\chi_n \to \chi^L$ in $L^2(\mathbb{R}^3, d^3r)$
3. $\chi_n(r)$ is bounded away from zero for $r < a_0/n$.

We then define the potentials $V_n(r)$ by

$$ V_n(r) = \begin{cases} 
\chi_n^{-1}\Delta\chi_n - \gamma/r & \text{for } r < a_0 \\
0 & \text{for } r > a_0.
\end{cases} \quad (6.5) $$

It is easy to see that the $V_n \in \mathcal{V}$ and so $\{H_n\}$ given by $H_n = -\Delta + \gamma/r + V_n(r)$ is an element of $\Sigma$. Furthermore, each term in the sequence has scattering length $L$. It is clear that $H_n\chi_n = H^L\chi^L$ for all $n$ (for within radius $a_0$, both sides
vanish, whilst for \( r > a_0 \), \( \chi_n \) and \( \chi^L \) are equal, and \( H_n \) and \( H^L \) have the same action). Moreover, because \( \chi_n \to \chi^L \), the strong graph limit of the \( H_n \) contains \( \langle \chi^L, H^L \chi^L \rangle \). By our remarks above, this suffices to prove that \( H_n \to H \) in the strong resolvent sense. \( \square \)

Next, we consider the situation when we restrict from \( \Sigma \) to \( \Sigma^+ \) and prove Theorem 3.2 (We defer the proof of Theorem 3.1 to the end of this section.)

**Theorem 3.2** All sequences in \( \Sigma^+ \) converge in the strong resolvent sense to \( H^0 \), the self-adjoint extension of \( H_{\text{ideal}} \) with regular boundary conditions.

**Proof:** Let \( H_n \) be a sequence in \( \Sigma^+ \). In exactly the same way as in the proof of Theorem 2.1(b), to show that \( H_n \to H^0 \), it is enough to show that \( \langle \chi^0, H^0 \chi^0 \rangle \) is contained in the strong graph limit of the \( H_n \), where \( \chi^0 \) is the mollified zero energy wavefunction of \( H^0 \). To prove this, let \( \psi_n \) be the generalised zero energy wavefunctions for the \( H_n \), normalised such that \( \psi_n(r) = r^{-1}(\phi(r) - L_n \theta(r)) \) for \( r > a_n \), where \( a_n \) is the radius of support and \( L_n \) the scattering length of \( V_n \). Then \( \chi_n(r) = g(r)\psi_n \) is in \( L^2(\mathbb{R}^3, d^3r) \).

Moreover, \( \chi_n \in D(H_n) \) for all \( n \) and

\[
H^0 \chi^0 - H_n \chi_n = L_n r^{-1} (g'' \theta + 2g' \theta') \vartheta(r-a_n)
\]

where \( \vartheta(x) \) is the Heaviside function. Thus, because the term in parentheses is smooth and compactly supported, this tends to zero, since, by Theorem 1.2, \( 0 \leq L_n \leq \phi(a_n) / \theta(a_n) \to 0 \). Thus \( H_n \chi_n \to H^0 \chi^0 \).

It therefore remains to show that \( \chi_n \to \chi^0 \). We know that \( \chi^0 - \chi_n = L_n g(r) r^{-1} \theta(r) \) for \( r > a_n \) and that \( g(r) r^{-1} \theta(r) \) has finite norm. Hence

\[
\int_{a_n}^{\infty} |\chi^0(r) - \chi_n(r)|^2 r^2 dr \to 0
\]

as \( n \to \infty \). Furthermore, for positive potentials, we know from the proof of Theorem 1.2 that \( r \chi_n(r) \) is increasing in \( r \) on \( (0, a_n) \) for sufficiently small \( a_n \), which implies that \( |r \chi_n(r)| \) is bounded above by \( \phi(a_n) - L_n \theta(a_n) \) on this interval and hence that \( \int_0^{a_n} |\chi_n - \chi^0|^2 r^2 dr \leq \int_0^{a_n} (|r \chi(r)|^2 + |r \chi_n(r)|^2) dr \to 0 \).

We therefore have \( \chi_n \to \chi^0 \), which entails that \( \langle \chi^0, H^0 \chi^0 \rangle \) is in the strong graph limit of the \( H_n \), yielding the required result. \( \square \)

As we noted in Section 2, whilst motivating the choice of strong resolvent convergence, the spectrum cannot expand in the limit of strong resolvent convergence. The precise statement of this result is:

**Proposition 6.5** (Theorem VIII.24(a) in [15]) Let \( \{A_n\} \) and \( A \) be self-adjoint and suppose \( A_n \to A \) in the strong resolvent sense. Then if \( \lambda \in \sigma(A) \), there exist \( \lambda_n \in \sigma(A_n) \) such that \( \lambda_n \to \lambda \).

This proposition allows us to prove Theorem 5.3.
Theorem 5.3 Suppose $\ell \geq 1$ and let $\lambda$ be an element of the spectrum of $\bar{h}_\ell$. Given $\epsilon > 0$, there exists a radius $a_\ell(\lambda, \epsilon) > 0$ such that, for any potential $V \in \mathcal{V}$ supported within $[0, a_\ell(\lambda, \epsilon))$

$$\text{dist}(\lambda, \sigma(h_{\ell, \text{true}})) < \epsilon$$

(6.8)

where $h_{\ell, \text{true}} = \bar{h}_\ell + V$ and $\text{dist}(x, Y) = \inf_{y \in Y} \|x - y\|$. 

Proof: Suppose otherwise. Then one could construct a sequence $V_n(x)$ of potentials in $\mathcal{V}$ with $V_n$ compactly supported within $[0, a_0/n]$, and hence a sequence of operators $h_{\ell, n} = \bar{h}_\ell + V_n(x)$ such that $\text{dist}(\lambda, \sigma(h_{\ell, n})) \geq \epsilon$ for all $n$. But it is clear that the strong graph limit of this sequence contains the graph of $\bar{h}_\ell$ restricted to $C^\infty_0(0, \infty)$, on which it is essentially self-adjoint. By Proposition 6.2, therefore, we have $h_{\ell, n} \to \bar{h}_\ell$. Proposition 6.3 shows that there must therefore exist a sequence $\{\lambda_n\}$, with $\lambda_n \in \sigma(h_{\ell, n})$ and $\lambda_n \to \lambda$. But this contradicts the fact that $\text{dist}(\lambda, \sigma(h_{\ell, n})) \geq \epsilon$ for all $n$ by construction. □

We conclude with the proof of Theorem 5.1, which includes Theorem 3.1 as a special case. This requires some more definitions. We write $Q(A)$ for the quadratic form domain of an operator $A$ and employ the usual abuse of notation by writing $\langle \phi \mid A\psi \rangle$ for the value of the quadratic form associated to $A$ acting on $\phi, \psi$. By $\mu_n(A)$, we denote (if it exists) the $n$’th eigenvalue of a self-adjoint operator $A$ which is bounded from below, counting in increasing order and with multiplicity.

We shall use the min-max principle (Theorem XIII.2 in [17]) to determine the eigenvalues of the operators at hand. Specifically, for $A$ a self-adjoint operator bounded from below, define

$$\nu_n(A) = \sup_{\varphi_1, \ldots, \varphi_{n-1}} \inf_{\psi \in U_A(\varphi_1, \ldots, \varphi_{n-1})} \langle \psi \mid A\psi \rangle$$

(6.9)

with

$$U_A(\varphi_1, \ldots, \varphi_m) = \{\psi \mid \|\psi\| = 1, \psi \in Q(A), \psi \in [\varphi_1, \ldots, \varphi_m]^\perp\}$$

(6.10)

where $[\varphi_1, \ldots, \varphi_m]$ denotes the linear span of $\varphi_1, \ldots, \varphi_m$. The min-max principle states that, for each $m$, either there are at least $m$ eigenvalues $\mu_1(A), \ldots, \mu_m(A)$ of $A$ given by $\mu_r(A) = \nu_r(A)$ for $r = 1, \ldots, n$ below the essential spectrum of $A$, or $\nu_n(A) = \inf \sigma_{\text{ess}}(A)$ in which case there are at most $n - 1$ eigenvalues below the essential spectrum given by $\mu_r(A) = \nu_r(A)$ for $r = 1, \ldots, n - 1$ and $\nu_m(A) = \inf \sigma_{\text{ess}}(A)$ for all $m \geq n$. Thus if $A$ has infinite discrete spectrum below the essential spectrum (which holds for the operators we consider) these eigenvalues are given directly by the min-max principle. In order to compare the eigenvalues of operators on different Hilbert spaces (as required for Theorems 3.1 and 5.1) we make the following definition, which is a mild extension of a definition in Section XIII.2 of [17].
Definition 6.6 Let $A$ and $B$ be self-adjoint and bounded below on Hilbert spaces $\mathcal{H}_1, \mathcal{H}_2$ respectively, where $\mathcal{H}_2$ is isometrically embedded in $\mathcal{H}_1$ by $\mathcal{J}$. We write $A \leq B$ if and only if $\mathcal{J}Q(B) \subseteq Q(A)$ and $\langle \mathcal{J}\psi \mid A\mathcal{J}\psi \rangle_{\mathcal{H}_1} \leq \langle \psi \mid B\psi \rangle_{\mathcal{H}_2}$ for all $\psi \in Q(B)$.

As an immediate consequence of this definition and the min-max principle, we have (cf. Section XIII.2 in [17])

Proposition 6.7 Let $A$ and $B$ be self-adjoint and bounded below on Hilbert spaces $\mathcal{H}_1, \mathcal{H}_2$ respectively, where $\mathcal{H}_2$ is isometrically embedded in $\mathcal{H}_1$ by $\mathcal{J}$. If $A \leq B$ then $\nu_n(A) \leq \nu_n(B)$ for each $n$.

Theorems 3.1 and 5.1 turn on the following lemma. Recall that $\bar{h}_0$ denotes $h_0^0$, the S-wave radial Hamiltonian with regular boundary conditions, which is bounded below.

Lemma 6.8 Let $h_{\ell,\text{true}} = \bar{h}_\ell + V$ for some positive $V(r) \in \mathcal{V}$, supported within $[0,a)$, for $a > 0$. For each $\ell = 0,1,2,\ldots$, the operators $\bar{h}_\ell, h_{\ell,\text{true}},$ and $h_\ell'$ are bounded below and $\bar{h}_\ell \leq h_{\ell,\text{true}} \leq h_\ell'$.

Proof: By hypothesis on the class of potentials $\mathcal{V}$ from which $V$ is taken, $Q(\bar{h}_\ell) = Q(h_{\ell,\text{true}})$, and since $V(r) \geq 0$, we have $h_{\ell,\text{true}}$ bounded below and $\bar{h}_\ell \leq h_{\ell,\text{true}}$ (we are in the special case of Definition 6.6 in which $\mathcal{H}_1 = \mathcal{H}_2$ and $\mathcal{J}$ is the identity). To prove the second inequality, let $\mathcal{J}$ be the isometry $\mathcal{J} : L^2([a,\infty),dr) \mapsto L^2(\mathbb{R}^+,dr)$ given by

$$\langle \mathcal{J}\psi)(r) = \begin{cases} 
\psi(r) & \text{for } r \geq a \\
0 & \text{for } r < a.
\end{cases} \quad (6.11)$$

$Q(h_\ell')$ is the set of $\psi$ such that

$$\int_a^\infty \left\{ \left| \frac{d}{dr} \psi \right|^2 + \left( \frac{\ell(\ell+1)}{r^2} + \frac{\gamma}{r} \right) |\psi|^2 \right\} dr < \infty \quad (6.12)$$

and it is clear that any such $\psi$ satisfies

$$\int_0^\infty \left\{ \left| \frac{d}{dr} \mathcal{J}\psi \right|^2 + \left( \frac{\ell(\ell+1)}{r^2} + \frac{\gamma}{r} \right) |\mathcal{J}\psi|^2 \right\} dr < \infty \quad (6.13)$$

as $\mathcal{J}\psi$ is continuous and piecewise once continuously differentiable on $\mathbb{R}^+$. Thus $\mathcal{J}Q(h_\ell') \subseteq Q(\bar{h}_\ell) = Q(h_{\ell,\text{true}})$. Clearly we have $\langle \mathcal{J}\psi \mid h_{\ell,\text{true}}\mathcal{J}\psi \rangle = \langle \psi \mid h_\ell'\psi \rangle$ for all $\psi \in Q(h_\ell')$, so $h_\ell'$ is bounded below and $h_{\ell,\text{true}} \leq h_\ell'$. $\square$

We now prove Theorem 5.1.

Theorem 5.1 For any $\ell$, let $h_{\ell,\text{true}} = \bar{h}_\ell + V$ for some positive $V \in \mathcal{V}$ with nuclear radius $a > 0$. Define $h_\ell'$ by (5.1) for this choice of $a$. Then $\bar{h}_\ell, h_{\ell,\text{true}}$ and $h_\ell'$ are bounded from below and possess infinitely many eigenvalues satisfying

$$\mu_r(\bar{h}_\ell) \leq \mu_r(h_{\ell,\text{true}}) \leq \mu_r(h_\ell') \quad (6.14)$$

for each $n = 1,2,\ldots$. 

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Proof: From Lemma 6.8 and Proposition 6.7, we have \( \nu_n(\bar{h}_\ell) \leq \nu_n(h_{\ell,\text{true}}) \leq \nu_n(h_\ell) \). \( \bar{h}_\ell \) has infinite discrete spectrum below its essential spectrum and in the Appendix, we show that the same is true for \( h'_{\ell,\text{true}} \), so the min-max principle gives \( \mu_n(\bar{h}_\ell) = \nu_n(\bar{h}_\ell) \) and \( \mu_n(h'_{\ell,\text{true}}) = \nu_n(h'_{\ell,\text{true}}) \). A further application of the min-max principle shows that \( h_{\ell,\text{true}} \) also has infinite discrete spectrum below its essential spectrum, thus yielding the required inequalities. \( \square \)

7 Conclusion

We first briefly consider the relation of the present paper to our work with Kay on the large scale effects of large objects in quantum mechanics [3]. More discussion is given in [2]. The ‘principle of sensitivity’ states that the fine details of a small object in the true problem (here the specific nuclear model chosen) can only change the large scale behaviour of the system if a family of idealised problems with differing large scale behaviour can be found. In the case in hand, we have seen in Section 2 that there is such a family of idealised problems in the \( S \)-wave, whilst for angular momenta \( \ell \geq 1 \), there is a unique idealised problem in each sector. Furthermore, Theorem 4.1 shows that true problems of arbitrarily nuclear radius can have spectra differing markedly from the Bohr levels in the \( S \)-wave, so there is good agreement with the principle of sensitivity in this sector. The situation for \( \ell \geq 1 \) is more subtle. We have seen (Corollary 5.4 to Theorem 5.3) that all true problems of sufficiently small nuclear radius preserve the Bohr levels to arbitrary accuracy; however, additional energy levels (termed ‘rogue eigenvalues’ in [3]) may also be introduced. There is, therefore, a sense in which the spectrum of the idealised problem is highly stable against general perturbations in these sectors, in accordance with the principle of sensitivity. Our considerations have thus demonstrated broad agreement with, and have clarified the scope of, the principle of sensitivity.

Our results in Section 5 also lead to an interesting viewpoint on the phenomenon of ‘accidental degeneracy’ [4, 8, 9, 10]; i.e. the fact that the Bohr levels for \( \ell \geq 1 \) are coincident with energy levels in the \( S \)-wave. This phenomenon is due to the conservation of the Laplace-Runge-Lenz vector, a symmetry of the idealised Hamiltonian with regular boundary conditions which is not shared by any true problem. If the nucleus is modelled by a positive correction to the Coulomb potential of small nuclear radius, Theorems 3.1 and 5.1 demonstrate that the degeneracy is approximately maintained. More generally one might expect that the degeneracy would be badly broken. Whilst the \( S \)-wave energy levels can indeed depart significantly from the Bohr levels, Theorem 5.3 provides the surprising result that degeneracy is maintained to arbitrary accuracy for the eigenvalues in \( \ell \geq 1 \) for all true problems of sufficiently small nuclear radius, modulo the presence of rogue eigenvalues. For angular momentum higher than zero, accidental degeneracy is no accident!
Our justification of the regular boundary condition was premised on the assumptions that the nuclear structure is spherically symmetric and can be modelled by a positive correction of compact support to the Coulomb potential. Theorem 5.2 indicates how the requirement of spherical symmetry may be relaxed. We also note that many non-everywhere-positive potentials have scattering lengths \( L \lesssim a \) (for instance, if the potential is ‘only slightly’ negative) and that one could therefore use the scattering length formalism of Section 4 to estimate the energy levels as being close to the Bohr levels. However to do this would necessitate a careful study of ‘believability’. It would be interesting to make rigorous statements about such cases and also to relax the requirement of compact support to allow, for example, exponentially decaying tails outside the nuclear radius.

To summarise: by identifying the different rôles of true and idealised problems in quantum mechanics, we have clarified the issue of which boundary conditions should be imposed at the Coulomb singularity of the idealised hydrogen atom. Under mild physical restrictions on the true problem, we have provided a rigorous justification for the regular boundary condition. Furthermore, we have developed a formalism for matching general true problems to (potentially) irregular boundary conditions, and have demonstrated that the entire 1-parameter family of boundary are required to model the full class of true problems, which (for arbitrarily small nuclear radius) can have \( S \)-wave energy levels differing markedly from the Bohr levels.

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Appendix: Spectral Properties of \( h'_{\ell} \)

In this appendix we prove the following statements concerning the spectrum of \( h'_{\ell} \) on \( L^2([a, \infty), dr) \) (recall that \( \mu_n(H) \) denotes the \( n \)'th eigenvalue of \( H \), counting in increasing order and with multiplicity, where \( H \) is self-adjoint and bounded below):

1. \( h'_{\ell} \) has infinite discrete spectrum below its essential spectrum \([0, \infty)\). Moreover, \( \mu_n(h'_{\ell}) \in [\mu_n(h_{\ell}), \mu_{n+1}(h_{\ell})] \).
2. In \( \ell = 0 \), \( \mu_n(h'_0) \leq \mu_{n+1}(h_{0}^{L_{\text{max}}}) \) where \( L_{\text{max}} = \phi(a)/\theta(a) \), provided \( a < a_1 \), where \( a_1 \) is the first non-trivial zero of \( \theta(r) \) away from the origin.
3. For \( a \ll a_0 \),
\[
\mu_n(h'_\ell) = -\frac{\gamma^2}{4(n + \ell + \xi_n)^2} \tag{A.1}
\]
for
\[
\xi_n \approx \frac{(n + 2\ell)!}{(2\ell + 1)!(2\ell)!(n - 1)!} \left( \frac{2}{n + \ell} \right)^{2\ell + 1} \left( \frac{a}{a_0} \right)^{2\ell + 1}. \tag{A.2}
\]

To prove these results, we first write \( u_\kappa(r) \) for the solution to
\[
-u'' + \left( \frac{\ell(\ell + 1)}{r^2} + \frac{\gamma}{r} \right) u = -\kappa^2 u \tag{A.3}
\]
on \( \mathbb{R}^+ \) such that \( u(r) \) is locally square integrable with measure \( dr \) as \( r \to \infty \), i.e., \( u(r) \propto \mathcal{W}_{r^2/(2\kappa^2)}(2\kappa r) \). Clearly, \( h'_\ell \) has eigenvalue \(-\kappa^2\) if and only if \( u_\kappa(a) = 0 \). Standard arguments give
\[
u_\kappa^2(a)u_\kappa''(a) - u_\kappa(a)u_\kappa''(a) = (\kappa_2^2 - \kappa_1^2) \int_a^\infty u_\kappa_1(r)u_\kappa_2(a)dr \tag{A.4}
\]
(the integral converges due to the boundary conditions on \( u_\kappa(r) \)). From this it follows that firstly, \( u_\kappa(a) \) has isolated zeros as a function of \( \kappa \), and secondly
\[
\frac{d}{d(\kappa^2)} \left( \frac{u_\kappa'(r)}{u_\kappa(r)} \bigg|_{r=a} \right) = -\frac{\int_a^\infty u_\kappa(r)^2dr}{u_\kappa(a)^2}. \tag{A.5}
\]
Hence \( u'_\kappa/u_\kappa |_{r=a} \) is increasing as a function of \( \kappa^{-1} \) between isolated poles, which correspond to eigenvalues of \( h'_\ell \). Now write \( v_\kappa \) for the solution to (A.3) with regular boundary conditions at \( r = 0 \). Clearly, \( h'_\ell \) has eigenvalues if and only if \( v'_\kappa/v_\kappa |_{r=a} = u'_\kappa/u_\kappa |_{r=a} \). Similar arguments to those above show that \( v'_\kappa/v_\kappa |_{r=a} \) is decreasing but everywhere positive as a function of \( \kappa^{-1} \). We conclude that between every two eigenvalues of \( h'_\ell \), there is exactly one pole of \( u'_\kappa/u_\kappa |_{r=a} \), and hence exactly one eigenvalue of \( h'_\ell \). Thus in particular, there are infinitely many negative eigenvalues.

Next, we know from Lemma 6.8 and Proposition 6.7 that \( \mu_n(h'_\ell) = \nu_n(h'_\ell) \leq \nu_n(h'_\ell) \) is determined by the min-max principle (see Section 6). By the min-max principle, \( \nu_n(h'_\ell) \) is either the \( n \)th eigenvalue below the essential spectrum, or the infimum of the essential spectrum. Hence \( \inf \sigma_{\text{ess}}(h'_\ell) \geq 0 \). However, if \( \nu_n(h'_\ell) = \inf \sigma_{\text{ess}}(h'_\ell) \) the min-max principle states that there are at most \( n - 1 \) eigenvalues below \( \inf \sigma_{\text{ess}}(h'_\ell) \). However, we have seen above that there are infinitely many negative eigenvalues, so \( \nu_n(h'_\ell) \) is the \( n \)th eigenvalue \( \mu_n(h'_\ell) \).

Putting this with our earlier observation shows that \( \mu_n(h'_\ell) \in [\mu_n(h'_\ell), \mu_{n+1}(h'_\ell)] \). That \( \sigma_{\text{ess}}(h'_\ell) = [0, \infty) \) may be seen by an explicit consideration of the generalised eigenfunctions.

To prove the second statement, we define \( r_L(\kappa) \) to be the position of the first zero (away from \( r = 0 \)) of the generalised eigenfunction of \( h^L \) at energy \(-\kappa^2\).
By arguments similar to the St"urm oscillation lemma one can see that $r_L(\kappa)$ is increasing continuously in $\kappa$. Moreover, $r_0(0) = a_1$, so $r_0(\kappa) > a$ for all $\kappa$. Inverting, we define $L(\kappa)$ to be such that $r_L(L_0(\kappa)) = a$. Then $L(\kappa)$ is decreasing in $\kappa$ where it is defined, and, by the fitting formula (4.7), $L(0) = L_{\text{max}} = \phi(a)/\theta(a)$, which is strictly positive for $a < a_1$. Moreover, because $r_0(\kappa) > a$ for all $\kappa$, $L(\kappa)$ cannot vanish and so remains in $(0, L_{\text{max}}]$. It is clear that $L(0)$ has an eigenvalue if and only if $L_0(\kappa)$ does, and also that $\mu_n(L_0(\kappa)) = \mu_{n+1}(L_{\text{max}})$ because $\mu_{n+1}(L_0(\kappa))$ is the eigenvalue of $L_0(\kappa)$ between $\mu_n(h_0)$ and $\mu_{n+1}(h_0)$. But we also know that $\mu_m(h_0L(\kappa)) \leq \mu_m(h_{\text{max}}L_0)$, so the second statement is proved.

To prove the third statement, note that it is enough to determine those values of $\kappa$ for which $u_\kappa(a)$ above vanishes. Now $u_\kappa(a)$ may be written

$$ u_\kappa(a) = e^{-\kappa a}(2\kappa a)^\ell+1 \Psi(\ell + 1 + \gamma/2\kappa, 2\ell + 2; 2\kappa a) $$

(A.6)

where $\Psi(a, c; z)$ is the irregular confluent hypergeometric function [18], so it is enough to find the zeros of $\Psi(\ell + 1 + \gamma/2\kappa, 2\ell + 2; 2\kappa a)$. We look for solutions in the neighbourhood of the Bohr levels $-\gamma/2\kappa = n + \ell$ for $n = 1, 2, \ldots$. Writing $-\gamma/2\kappa = n + \ell + \xi$ and expanding in powers of $\xi$, we find

$$ \Psi(\ell + 1 + \gamma/2\kappa, 2\ell + 2; 2\kappa a) = \Psi(1 - n, 2\ell + 2; 2(n + \ell - 1)a/a_0) + K(\ell, n, a/a_0)\xi + O(\xi^2) $$

(A.7)

where

$$ K(\ell, n, \delta) = -\Psi'(1 - n, 2\ell + 2, 2\delta(n + \ell)) $$

$$ + 2\delta \frac{(1 - n)}{(n + \ell)^2} \Psi(2 - n, 2\ell + 3, 2\delta(n + \ell)) $$

(A.8)

and $\Psi'(a, c; z) \equiv (\partial/\partial a)\Psi(a, c; z)$. Working to lowest order in $a/a_0$, we find

$$ \Psi(\ell + 1 + \gamma/2\kappa, 2\ell + 2; 2\kappa a) \approx (-1)^{n-1} \frac{(n + 2\ell)!}{(2\ell + 1)!} $$

$$ -\xi(-1)^{n-1} (n - 1)! (2\ell)! \left(\frac{2}{n + \ell a_0}\right)^{(2\ell+1)} $$

(A.9)

and so we find the approximate solutions given in our third statement.


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Figure Captions:

Figure 2.1: The function $G(z)$. 