Nonrelativistic effective quantum mechanics of the Coulomb interaction

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Abstract

We apply the ideas of effective field theory to the nonrelativistic quantum mechanics of the Coulomb problem. Utilizing an artificial boundary of ignorance as a calculational tool, we develop this effective theory using boundary conditions to encode short-ranged effects that are deliberately not modeled; thus, the boundary conditions play a role similar to the effective action in field theory. We find that this effective theory can predict the bound state energies of hydrogen-like systems to very high accuracy with a small number of fitting parameters. It is also shown to be equivalent to the theory of quantum defects, but derived here using an effective framework. The method respects electromagnetic gauge invariance and also can describe decays due to short-ranged interactions, such as those found in positronium. Potential applications of this approach include atomic and condensed matter systems that admit analytic long-range descriptions, but whose short-ranged effects are not reliably or efficiently modeled. It may also provide a useful perspective for the study of blackholes.

1. Introduction

Effective field theory (EFT) has had many successes dating back at least as early as Fermi’s model of the weak-interaction [1], through modern implementations in condensed matter and particle physics [2–41, gravitation [5], as well as cosmology and astrophysics [6–10]. The success of an effective field theory depends on a hierarchy of scales; the momenta or wavelengths of the experimental probes or observations of a system must be markedly different from the scale(s) of the processes not described, at least in detail, by the effective theory; see, e.g., [11] for a review on EFT.

In this work we apply many of the ideas of EFT to quantum mechanics. The starting point of our discussion begins with the description of contact interactions, or delta-function potentials, in quantum mechanics in two and three dimensions. It is known that such potentials sometimes require elaborate regularization and renormalization schemes to ensure physically sensible results are obtained [12]. In [12] it was advocated that non-trivial boundary conditions are a preferable alternative method to using delta functions.

When applied to bound Coulomb states, this non-trivial boundary condition method—also known as the method of self-adjoint extension—has been shown to produce energy levels that obey Rydberg’s formula, at least when the boundary condition parameter is small and proportional to the quantum defect [13]. In [13] it was shown that a unique boundary condition can provide an effective description of ‘UV’ physics near the origin, such as the effect of a finite nuclear radius or anything that may be approximated as a delta-function potential. There are two notable limitations to the analysis in [13]: (1) because all non-trivial \( \ell \neq 0 \) solutions to the Schrödinger equation are not normalizable, the method applies only for \( S \)-states (\( \ell = 0 \)) and (2) it does not reproduce the Rydberg-Ritz formula, the more accurate bound state energy formula in which the quantum defect is energy-dependent [14, 15].

The motivation of [16] was to extract a useful effective theory that would apply for all angular momentum states. In that work a finite region of space encompassing the origin was omitted from analysis, thereby naively obviating the need to discard the non-trivial \( \ell \neq 0 \) solutions. The radius of what is referred to as the boundary of
ignorance, $r_b$ was interpreted as a kind of short-distance cutoff—alognus to an ultraviolet cutoff in EFT—on which the boundary conditions effectively parameterize the omitted short-ranged interactions. In order to enforce strict probability conservation, however, the limit $r_b \to 0$ had to be taken at the end of any calculation; it follows that the analysis of [16] only reproduces the results of [13]. Thereafter, results in [17, 18] demonstrated similar results using an effective field theory of point particles.

In [19], it was realized that violation of unitarity is not necessarily a problem if the violation is only temporary because the norm of a state function averages to unity. Therefore, it is not necessary to take the limit $r_b \to 0$ to arrive at a useful theory. From another point of view, one should not need to have a complete description of a system to arbitrarily short distance from the origin, just as the framework of EFT does not require a complete understanding of a theory to arbitrarily large momentum.

To briefly recap the results of [19], recall that for a one-dimensional system described by a scalar potential and a boundary at the coordinate $x = x_b$, all eigenmodes must obey the same (Robin) boundary condition in a standard analysis, i.e.

\[
\psi_i(x_b) + Z \psi'_i(x_b) = 0,
\]

where the modes are labelled by generic index $i$, and $Z$ is a real number; for example, $Z = 0$ corresponds to the Dirichlet condition. The central equation of [19] is what results from promoting the boundary condition to be mode-dependent, i.e. $Z \to Z_i$, or

\[
\psi_i(x_b) + Z_i \psi'_i(x_b) = 0.
\]

Because the boundary condition varies for different eigenmodes, this theory is not instantaneously hermitian or unitary; however, those standard conditions do hold when averaged over sufficiently long times \(^3\).

In this article we extend the analysis of [19], demonstrating that this approach can be successfully applied in three dimensions with coupling to the full electromagnetic gauge field. We devote our efforts to analysis of hydrogenic atoms and arrive at the theory of quantum defects, albeit using a different framework from earlier analyses (see, e.g., a well-known review by Seaton [15]). The theoretical framing here is in the same spirit as that of effective field theory; however, we do not appeal to a Lagrangian formalism. We start with the Schrodinger equation, using a Hamiltonian valid at long distance, while the conditions of the wavefunction on the boundary of ignorance play a role analogous to the effective action in EFT. We therefore consider this method to be a demonstration of what can be called effective quantum mechanics.

In section 2 we derive the three-dimensional version of the boundary condition (2) that respects electromagnetic gauge invariance and discuss its consequences. In section 3 we analyze the bound states of the Coulomb problem and derive the theory of quantum defects. In section 4 we check the effective method against synthetically-generated data for a UV-complete model of an extended nucleus. In section 5 we consider the successes and limitations of this non-relativistic theory applied to real systems. In section 6 we consider decaying states. In section 7 we conclude with a discussion of our results, list possible applications, and mention some outstanding issues. Throughout this article we use the natural unit convention $\hbar = c = 1$.

2. Boundary condition and consequences

The dynamics of a point charge of mass $m$ and charge $Q$ coupled electromagnetically is described by the Hamiltonian

\[
H = \frac{(\vec{p} - QA)^2}{2m} + Q\varphi,
\]

which yields a Schrodinger equation that is gauge-invariant under the local transformation of the wave function and the electromagnetic field characterized by the function $\Omega$,

\[
\Psi = e^{iQ\Omega} \psi', \\
\vec{A} = \vec{A}' + \nabla \Omega, \\
\varphi = \varphi' - \Omega.
\]

We derive a spherically-symmetric, gauge-invariant analogue to (2) by considering the flow of probability associated with a single eigenmode where, for simpler notation, we note that $\Psi$ represents such a mode. Here we allow for the possibility that the eigenmode in question decays at a rate, $\Gamma$, via some interaction(s) near the

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\(^3\) Unitarity violation is consistent with a theory that only considers the domain $x \geq x_b$, whereas a particle can, in reality, propagate in and out of the omitted region, $0 \leq x < x_b$. 

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origin\(^4\). In other words, normalizing the state at \(t = 0\),

\[
\frac{d}{dt} \langle \Psi, \Psi \rangle = - \int dV \nabla \cdot \vec{J} = - \Gamma e^{-\Gamma t},
\]

where the probability current density \(\vec{J}\) following from the Hamiltonian \((3)\) is

\[
\vec{J} = \frac{i}{2m} [ (\nabla \Psi^*) \Psi - \Psi^* (\nabla \Psi) + 2iQA |\Psi|^2].
\]

We assume the eigenmodes may be written in the variable-separated form as

\[
\Psi = e^{-i\omega t - \frac{\Gamma}{2} \int dV Y m(\theta, \phi)}.
\]

The divergence theorem may be used to demonstrate that

\[
(D_{\Gamma} R)^* R - R^* D_{\Gamma} R_{\mid r = r_0} = \frac{2im}{r_0^2} \Gamma.
\]

where

\[
D_{\Gamma} = \partial_r - iQA_r,
\]

and \(A_r\) is the radial component of the potential, \(\bar{A}\).

Following \([20]\), one may then multiply equation \((8)\) by an arbitrary function \(w(r_b)\), which has units of length, and define the dimensionless complex quantities

\[
x \equiv R(r_b) \quad \quad \quad \quad y \equiv wD_{\Gamma} R(r)|_{r = r_b},
\]

It may be verified that equation \((8)\) is therefore equivalent to

\[
\left| x + iy \left( 1 - \frac{mw\Gamma}{r_b^2} |y|^2 \right) \right|^2 = \left| x - iy \left( 1 + \frac{mw\Gamma}{r_b^2} |y|^2 \right) \right|^2.
\]

Because there is an equivalence of the arguments up to an arbitrary phase factor \(e^{i\theta}\), where \(0 \leq \theta < 2\pi\), it follows that

\[
R = \left( \cot \frac{\theta}{2} w + \frac{m\Gamma}{r_b^2 |D_{\Gamma} R|^2} \right) D_{\Gamma} R = 0.
\]

The boundary condition may then be written in the form

\[
R(r_b) + \mathcal{Z}(r_b) D_{\Gamma} R(r_b) = 0,
\]

the desired analogue of \((2)\), where

\[
\text{Re} \left[ \mathcal{Z}(r_b) \right] = \mathcal{Z}_{\text{re}}(r_b) = - \cot \frac{\theta}{2} w,
\]

and

\[
\text{Im} \left[ \mathcal{Z}(r_b) \right] = \mathcal{Z}_{\text{im}}(r_b) = - \frac{m\Gamma}{|r_b D_{\Gamma} R|^2}.
\]

Again, we note that \(\theta, w\) and, therefore, \(\mathcal{Z}\) are unique to the specific eigenmode in question. While \(\theta\) and \(w\) do not separately have a simple physical interpretation, their combination in the form of \(\mathcal{Z}\) acts as a dimensionful coupling constant associated with the interactions that may occur behind the boundary of ignorance.

There are consequences of promoting the boundary condition to be mode-dependent—even when \(\Gamma = 0\) it appears that unitarity is violated. However, such a violation is only temporary in nature; probability is conserved when averaged over sufficiently long times, as discussed in \([19]\). Precisely what is considered sufficiently long depends on the physical system being studied. Because we focus exclusively on Coulomb bound states in the sections below, let us consider a composite state built from two such eigenmodes, \(i\) and \(j\), with the same angular quantum numbers. Averaging over a time much longer than \(\pm \frac{2\Gamma}{|\omega - \omega|} w^2\) is sufficient to demonstrate that probability is conserved, according to the analysis in \([19]\), and this is always larger than the time scale associated with any omitted short-distance phenomena. The averaging time must also be much shorter than any processes not included in this analysis that occur over relatively long times, such as the spontaneous transition time between the two states, which is also true\(^5\). Although this by no means constitutes a proof that this method will

\[4\] This effective method can describe decays of states due to short-ranged effects, such as annihilation; this analysis does not describe, e.g., transitions from one Coulomb state to another.

\[5\] The transitions between states with the same angular momentum are accompanied by the emission of at least two photons. Such processes occur at a rate that does not exceed \(\sim |\omega_i - \omega_j| \alpha^2\) (see, e.g., \([21]\)).
work for all systems, it does suggest that its success as an effective theory depends on a clear hierarchy of time scales, in addition to length scales.

### 3. Coulomb states

Here we limit ourselves to systems in which $\Gamma = 0$ and consider an electron of charge $-e$ bound to a positive nucleus of charge $Ze$, so that the long-distance Hamiltonian is given by equation (3) with $A = 0$ and scalar potential

$$& \varphi = \frac{Ze}{r}.$$  

The time-independent radial Schrödinger equation is

$$& -\frac{1}{r^2} \partial_r (r^2 R(r)) + \left( \frac{\ell (\ell + 1)}{r^2} - \frac{2\kappa}{r} + q^2 \right) R(r) = 0$$  

where

$$& \kappa = Zm\alpha,$$

$\alpha \approx 1/137$ is the fine structure constant, and the energy eigenvalues are defined by

$$& E = -\frac{q^2}{2m}.$$  

As described in [16] there is one independent solution to this differential equation that is guaranteed to be square-integrable in the $r \to \infty$ limit. We write this as, up to a normalization constant,

$$& R(r) = e^{-\varphi} (2qr)^{\ell} \left( U + \ell - \frac{\kappa}{q}, 2(\ell + 1), 2qr \right),$$

where $U$ is Tricomi’s confluent hypergeometric function.

Quantization of the energies comes from application of the boundary condition (14). It must be obeyed in such a way that any observables, such as the energy or, equivalently, $q$ are independent of the location of the boundary. Because this is a long-distance effective theory, we expect the spatial scale of the wavefunction to be much larger than the boundary radius, or $qr_b \ll 1$. This means that, in principle, equation (14) could be expanded to arbitrary order in $qr_b$ and would then provide an arbitrarily precise analysis. Any function of $q$ could then be solved for; in particular, we find it best to solve for $\psi \left( 1 + \ell - \frac{\kappa}{q} \right)$, where

$$& \psi(z) = \frac{\Gamma'(z)}{\Gamma(z)};$$

is the digamma function and $\Gamma(z)$ is the gamma function.

The digamma function is readily seen to appear in the series form of the Tricomi function; see, e.g., [22]. By using the digamma identity,

$$& \psi(1 + z) = \psi(z) + \frac{1}{z},$$

one could in principle solve equation (14), accurate up to a particular order in the expansion parameter, $qr_b$, and write

$$& \psi \left( 1 + \ell - \frac{\kappa}{q} \right) = F_\ell \left( Z(r_b), r_b \right),$$

where $F_\ell$ is a function of both the boundary function $Z(r_b)$ and the boundary radius, $r_b$. Because $q$ must not depend on the location of the boundary, it can be said that $Z(r_b)$ runs, in the sense of the renormalization group, with $r_b$ in a way that ensures that the eigenvalues do not depend on it; this was first described in [16], but a similar procedure may be found in [17]. However, it is more straightforward to simply note that the right hand side of (24) must be equal to some $r_b$-independent integration function, which we call $\chi_\ell(q)$. This establishes the result

$$& \psi \left( 1 + \ell - \frac{\kappa}{q} \right) = \chi_\ell(q).$$

One of us (D.M.J.) would like to acknowledge Harsh Mathur for explaining the importance of this particular (decaying) linear combination of the two solutions to the confluent hypergeometric equation.
As in [19], we posit that $\chi_\ell(q)$ captures the unspecified interactions behind the boundary, $r < r_b$. We follow this procedure because, in practice, solving explicitly for $\mathcal{Z}(r_b)$ is cumbersome even at lowest order in the $a r_b$ expansion and for $\ell' = 0$; it becomes increasingly challenging at higher order and at higher values of $\ell'$. Instead, given the series form of the Tricomi function [22] and boundary condition (14) that must be satisfied for arbitrary $r_b$, we make the generic ansatzootnote{An arbitrary choice of length of $(2\kappa)^{-1}$ was put into the argument of the logarithm; any other choice can be made with a corresponding redefinition of the $\boldsymbol{c}$'s.} for the boundary function,

$$
\mathcal{Z}(r_b) = \kappa^{-1} \sum_{j=1}^{\infty} (c_j + d_j \ln 2\kappa r_b)(2\kappa r_b)^j.
$$

By solving (14) for each term proportional to $r_b^j$ and $\ln r_b r_b^j$ we can determine the dimensionless coefficients $c_j$ and $d_j$ uniquely, up to the arbitrary integration function $\chi_\ell(q)$ which must appear in any equation containing $\psi\left(1 + \ell' - \frac{\kappa}{q}\right)$. It may be verified that $\chi_\ell(q)$ only appears in the $c_j$ and does not first appear in the series until $\epsilon_{2\ell+2}$; it then appears in all subsequent $c_j$ which may be understood through use of the digamma identity (23).

Below we will not explicitly refer to $\chi_\ell(q)$, but its presence is implied in any discussion of $\epsilon_{2\ell+2}$, which we simply refer to as the integration function.

We do not, at present, have an analysis valid for arbitrary $\ell'$. However, we have checked that the following procedure works at least up to $\ell' = 3$; it therefore seems implausible that it would not work to arbitrarily high $\ell'$. We explicitly show the procedure for $\ell' = 0$ and $\ell' = 1$ below and the $\ell' = 2$ analysis may be found in appendix. The summary is that at each $\ell'$ we may write the solutions as deviations from their canonical form as

$$
q = \frac{\kappa}{n - \delta_\ell}
$$

where $n$ is an integer and $\delta_\ell$ is called the quantum defect (see, e.g., [15]). For each $\ell'$-state we have considered it is possible to write the defect in the form

$$
\delta_\ell = \delta_\ell(0) + \lambda_\ell(1) E^2 + \lambda_\ell(2) \left(\frac{E}{\Lambda}\right)^2 + \ldots,
$$

in other words, a low energy expansion in $E/\Lambda$, where $\Lambda$ is a high energy (UV) scale.

The connection between non-trivial boundary conditions and the leading quantum defect ansatz of (27) was first made in [13]. The ansatz for $q$, equation (27), is a deviation from the canonical solutions,

$$
q = \frac{\kappa}{n},
$$

and is motivated by two distinct considerations. The first reason is obvious: from an experimental point of view, hydrogenic atoms and highly excited (Rydberg) states of large atoms are known to display spectra that are largely in agreement with (29)—this was, of course, one of the earliest successes of quantum mechanics. This canonical case apparently corresponds to the limit $\chi_\ell \to \pm\infty$, suggesting that it or, equivalently, the $\epsilon_{2\ell+2}$ will actually take on very large (but finite) values when this method is applied to real systems.

The second reason to use the canonical solutions as a point of departure is that they are special from the theoretical point of view; they are the unique solutions for which there is exists an $n^2$-fold degeneracy at each energy level, $\kappa$. This can be traced to presence of a ‘hidden’ $SO(3) \otimes SO(3)$ symmetry, the result of a conserved Runge-Lenz vector, in addition to angular momentum (see, e.g., [23]). As deviations are made from the canonical solution (29), therefore, one could say that the $SO(3) \otimes SO(3)$ symmetry is broken to the usual $SO(3)$ symmetry associated with 3-dimensional rotations [13]. Although the Runge-Lenz vector operator continues to be conserved, the $\ell'$-dependent boundary conditions mean that it acts on a different domain than that of the Hamiltonian, making it an unphysical operatorootnote{See, e.g., [24] for a discussion about an analogous problem on a conical space in two dimensions.}.

### 3.1. Effective description of $\ell' = 0$ bound states

For the $\ell' = 0$ solutions, the term-by-term consideration of the boundary condition (14) with the ansatz of (26) yields

$$
\epsilon_2 = -\gamma - \frac{q}{4\kappa} - \frac{1}{2} \left[ \ln \frac{q}{\kappa} + \psi\left(1 - \frac{\kappa}{q}\right)\right],
$$

$$
\ell
$$

\begin{align}
\ell + 1 &= \ell + 1 \\
2\ell + 1 &= 2\ell + 1 \\
3\ell + 1 &= 3\ell + 1
\end{align}
where $\gamma$ is the Euler-Mascheroni constant. Performing an asymptotic expansion of the digamma function yields

$$c_2 = -\frac{\pi}{2} \cot \frac{\pi}{q} - \gamma - \frac{1}{24} \frac{E}{E_{\text{Ry}}} - \frac{1}{240} \left( E \frac{E}{E_{\text{Ry}}} \right)^2 + O \left( \frac{E}{E_{\text{Ry}}} \right)^3. \quad (31)$$

where

$$E_{\text{Ry}} \equiv \frac{\kappa^2}{2m}. \quad (32)$$

We make the ansatz

$$q = \frac{\kappa}{n - \delta} \quad (33)$$

where, as argued in [19], it should always be possible\(^{10}\) to define $|\delta| \leq 1/2$. It appears that this is the only departure from the original quantum defect model, wherein there is no such restriction on the size of the defect (see, e.g., [14]). We expand equation (31) in small $\delta$ and find that the defect can be solved for implicitly as

$$\delta = -\left( 1 - \frac{\pi^2}{3} \delta^2 - \frac{\pi^4}{45} \delta^4 + O(\delta^6) \right) \frac{2c_2}{2\gamma + \frac{1}{12} \frac{E}{E_{\text{Ry}}} + \frac{1}{120} \left( \frac{E}{E_{\text{Ry}}} \right)^2 + O \left( \frac{E}{E_{\text{Ry}}} \right)^3}. \quad (34)$$

We do not know what functional form the integration function—or $c_2$—should have, but two comments are warranted. Firstly, deviations from the canonical Coulomb spectrum are assumed here to be the result of short-ranged/slow-energy physics not included explicitly in the Coulomb potential, and therefore we expect those deviations not to depend explicitly on the ratio $E/E_{\text{Ry}}$. Secondly, a series form for $c_2$ as an expansion in $E$ over some high energy scale is arguably the simplest guess, and is also consistent with the well-known and successful approach taken when writing down an action in the context of effective field theory; thus we claim that the boundary condition—really the boundary function—plays a role similar to that of the effective action in EFT. Not knowing a priori what the coefficients of this expansion should be, we parametrize the denominator of equation (34) to be in the series form

$$A_0 + A_1 \frac{E}{\Lambda} + A_2 \left( \frac{E}{\Lambda} \right)^2 + ..., \quad (35)$$

where $\Lambda$ is a high energy scale and, in the parlance of EFT, we call the $A_i$ renormalized expansion coefficients. Equivalently, the integration function could apparently be written

$$c_2 = B_0 + B_1 \frac{E}{\Lambda} + B_2 \left( \frac{E}{\Lambda} \right)^2 + ..., \quad (36)$$

where the bare expansion coefficients, $B_i$ are related to their renormalized counterparts by

$$B_0 = \frac{A_0}{2} - \gamma$$

$$B_1 = \frac{A_1}{2} - \frac{1}{24} \frac{\Lambda}{E_{\text{Ry}}}$$

$$B_2 = \frac{A_2}{2} - \frac{1}{240} \frac{\Lambda^2}{E_{\text{Ry}}^2}, \quad (37)$$

and so on. Summarizing, we have

$$\delta = \left( 1 - \frac{\pi^2}{3} \delta^2 - \frac{\pi^4}{45} \delta^4 + O(\delta^6) \right) \frac{A_0 + A_1 \frac{E}{\Lambda} + A_2 \left( \frac{E}{\Lambda} \right)^2 + ...}{A_0 + A_1 \frac{E}{\Lambda} + A_2 \left( \frac{E}{\Lambda} \right)^2 + ...} \quad (38)$$

which can be iteratively solved for $\delta$. Without any loss of generality, we therefore write

$$\delta = \delta_0 + \lambda_1 \frac{E}{\Lambda} + \lambda_2 \left( \frac{E}{\Lambda} \right)^2 + ..., \quad (39)$$

9 Although this series does not converge, any truncation will be increasingly accurate as $|E|$ decreases.

10 In [19] the definition $n - \delta \equiv \tilde{n} - \delta$ was made, where $\tilde{n}$ is the closest integer to $n - \delta$, therefore $|\delta| < 1/2$ was guaranteed. In the interest of clarity we do not adopt that notation; instead we mandate $|\delta| < 1/2$. 
where $\delta_0$ and the $\lambda_i$ are dimensionless coefficients. One could speculate that, because $\delta \to 0$ as the canonical solutions are recovered, $\delta_0$ is proportional to $E_{Ry}/\Lambda$, possibly raised to a positive power. We demonstrate below that this is indeed the case, at least when applied to the hydrogen atom.

### 3.2. Effective description of $\ell' = 1$ bound states

Following the procedure used in the previous section, for $\ell' = 1$ we discover

$$
c_4 = \frac{9 - 16\gamma}{256} - \frac{3}{64\kappa} - \frac{(1 - \gamma)}{16} \frac{q^2}{\kappa^2} + \frac{1}{64\kappa^2}
+ \frac{q^2 - \kappa^2}{32\kappa^2} \left( \ln \frac{q}{\kappa} + \psi \left( \frac{2 - \kappa}{q} \right) \right).
$$

After expanding the digamma function in small $q/\kappa$ and writing this expression in terms of energies we find

$$
\delta = \frac{1}{32c_4} \cdot \left( 1 + \frac{E}{E_{Ry}} \right) \left( 1 - \frac{\kappa^2}{3} \delta^2 - \frac{\kappa^4}{45} + \mathcal{O}(\delta^6) \right)
- \frac{9 + 2\gamma}{8} \cdot \frac{11 - 24\gamma}{12} \cdot \frac{E}{E_{Ry}} + \frac{11}{120} \left( \frac{E}{E_{Ry}} \right)^2 + \mathcal{O}\left( \frac{E}{E_{Ry}} \right)^3.
$$

### 3.3. Brief comments about scattering

Because of the apparent equivalence between this effective approach and that of quantum defect theory, we do not dwell on the analysis of scattering states. We simply note that, whereas in bound state calculations the definition $q^2 = -2mE$ is made, for scattering one defines the wave number $k$ by

$$
k^2 = 2mE,
$$

where the energy, $E > 0$. This suggests an analytic continuation of the integration function $\chi_\ell(q^2)$ in the variable $q^2 \to -k^2$, in other words an analytic continuation of the defects $\delta_\ell(E)$ from $E < 0$ to $E > 0$. This is precisely what is known to occur within quantum defect theory and we direct the interested reader toward the relevant literature (see, e.g., [15] and references therein).

### 4. Fits to synthetic data

Here we consider the long-range Coulomb potential modified at short distance with a specific UV-completion, namely one in which there is a constant nuclear charge density. The scalar potential is therefore

$$
\varphi = \begin{cases}
\frac{Ze^2}{R_{\text{nuc}}^3}, & (0 \leq r \leq R_{\text{nuc}}) \\
\frac{Ze}{r}, & (r > R_{\text{nuc}}).
\end{cases}
$$
The time-independent radial Schrödinger equation in the nuclear interior is

\[-\frac{1}{r^2} \partial_r (r^2 R(r)) + \left( \frac{\ell (\ell + 1)}{r^2} - \frac{4r^2}{b^4} + q^2 \right) R(r) = 0, \tag{47}\]

where

\[b^4 \equiv \frac{2R_{\text{nuc}}^2}{Zm\alpha}. \tag{48}\]

Imposing regularity at the origin, the solution to (47) may be written, up to a normalization constant, as

\[R(r) = e^{-i\left(\frac{i}{2}\right)^{\ell + 1}} \left( \frac{\ell}{b} \right)^{\ell} \times \left( M \frac{2\ell + 3}{4} - \frac{iq}{8} \right)^4 \left( \frac{e}{b} \right)^2, \tag{49}\]

where \(M\) is Kummer’s hypergeometric function.

It is important to separately consider two different types of hydrogenic systems, namely those in which deviations from the Coulomb potential occur at a radius that is either smaller or larger than the Bohr radius. For this reason, we consider two examples in which the nuclear radius, \(R_{\text{nuc}}\) satisfies either or \(\kappa R_{\text{nuc}} < 1\) or \(\kappa R_{\text{nuc}} > 1\). The synthetic bound state energies of this UV-complete model are generated by matching the interior and exterior solutions, equations (21) and (49), and their first derivatives at \(r = R_{\text{nuc}}\).

To display the robustness of the effective theory we apply it to bound states with a leading order (LO) fit using only \(\delta f(0)\), next-to-leading order (NLO) by fitting for \(\delta f(0)\) and \(\lambda\), next-to-next-to leading order (NNLO) by fitting for \(\delta f(0)\), \(\lambda\), and \(\lambda\). We assume both \(m\) and \(\alpha\) are perfectly known by some independent means, and utilize equations (20), (27), and (28) to fit to the lowest energy levels, i.e. those with the largest \(|E|\), so as to make predictions for the higher energy levels.

In figures 1 and 2 we display the relative error in the predicted energy levels for \(\kappa R_{\text{nuc}} = 0.31\) when \(\ell = 0\) and \(\ell = 1\), respectively; in those figures we normalize the energies to the ground state, \(E_0\).

For the large nuclear radius, we choose \(\kappa R_{\text{nuc}} = 2.73\). The method here is unsuccessful unless one fits the effective theory to the synthetic data starting at somewhat higher energy levels. This is consistent with the fact that this method is a long-distance effective theory; thus, one should only expect it to provide accurate predictions when the characteristic length scale of the wavefunction is large compared to the nuclear radius, or \(q R_{\text{nuc}} < 1\). We choose not to fit the first 20 synthetic levels (ground state and 19 excited states), beginning our fits near the canonical eigenvalue of \(q = \kappa/21\) and, therefore, make predictions beginning near \(q = \kappa/22\). In figures 3 and 4 we display our results for \(\ell = 0\) and \(\ell = 1\), respectively, normalizing the energies to the 21st excited state, \(E_{21}\). Although the errors initially grow marginally as higher energy levels are considered, eventually there is a turnover, and the errors begin to decrease. In any case, at any given energy level, the effective method gives predictions that are always more accurate at higher order.

5. Application to physical systems

In so far as Rydberg atoms are concerned, the \(\delta\) ansatz of (28) is equivalent to the usual quantum defect method (s), wherein the modified Rydberg-Ritz expression is often written...
for some experimentally determined constants $\delta_0, \delta_2, \text{etc}$ [14]. The only difference with our approach, as mentioned in section 3.1, is that here we restrict the size of the defect to obey $|\delta_0| < 1$. For example, the measured transition frequencies of the alkalis $^{23}\text{Na}$, $^{39}\text{K}$, and $^{85}\text{Rb}$ are fit with the original defect model to give a leading order $s$-state defect, $\delta_0^{\text{QDT}} \approx 1.380, 2.180$ and $3.131$, respectively [14]. In the effective model these are simply interpreted as $\delta_0 = 0.380, 0.180$, and $0.131$. In other words, the ground state of an alkali atom corresponds to $n = 1$, rather than the principal quantum number corresponding to its row in the periodic table.

However, there are limitations to the method presented here and, therefore, to quantum defect theory itself. This is perhaps most easily established by attempting to apply this effective theory to the hydrogen spectrum. One can achieve reasonably accurate results with the hydrogen atom; however, the predictions become only marginally more accurate at higher order in the effective theory, and this is likely because of relativistic effects that are not accounted for. Consider that, at leading order, $\delta_0 = \delta_0^{\text{QDT}}$, so that, expanding in small $\delta_0$, the energy levels are

$$\delta_{n\ell} = \delta_0 + \frac{\delta_2}{(n - \delta_0)^2} + \frac{\delta_4}{(n - \delta_0)^4} + \ldots,$$

(50)
The first term corresponds to the canonical eigenvalues, whereas the second term is proportional to the corrections that are usually obtained using perturbation theory; in particular, short-ranged corrections to the Coulomb potential, such as spin-orbit and spin-spin couplings, which are proportional to \(1/r^3\) or a delta-function centered about \(r = 0\), give corrections proportional to \(n^{-3}\) (see, e.g., [25]). Let us call those potential corrections \(U_{\text{rel}}\). Perturbation theory is used to correct the canonical energy levels by an amount

\[
\langle \Psi | U_{\text{rel}} | \Psi \rangle = - \frac{m\alpha^4}{(2j + 1)n^3},
\]

where \(j = \ell' \pm 1/2\) [26]. Matching with the effective method indicates that

\[
\delta_{\ell(0)} = \mathcal{O}(\alpha^2),
\]

or \(\delta_{\ell(0)} \propto E_{\text{Ry}}/\Lambda\), which is true when we set the high energy scale \(\Lambda = m\), the mass of the electron.

At the next-to-leading order, we apparently have

\[
\delta' = \delta_{\ell(0)} - \lambda_{\ell(1)} \frac{\alpha^2}{2n^2}.
\]

With an additional parameter there is, of course, an improved fit to the hydrogen spectrum; however, it is only a marginal improvement. Although equation (51) is modified, the effect of the parameter \(\lambda_{\ell(1)}\) only appears at order \(n^{-5}\), whereas there is already trouble with the order \(n^{-4}\) term. This is because there is a remaining fine-structure effect not captured by \(U_{\text{rel}}\) but instead comes from the relativistic correction to the kinetic energy. That kinetic correction amounts to

\[
\frac{3m\alpha^4}{8n^4}
\]

for all \(\ell\) states of Hydrogen, and this cannot be accounted for simultaneously with the order \(n^{-3}\) correction in equation (52). In any case it would not be appropriate; the relativistic kinetic energy correction is not a short-ranged effect that can be hidden behind a boundary of ignorance.

Although this and the preceding sections demonstrate the utility of the non-relativistic effective quantum mechanics, a relativistically corrected version of the theory is clearly warranted. Some progress in this direction was made in [27], which focused on positronium.

6. Decays due to UV effects

As a concrete example of a hydrogen-like system that decays due to short-ranged effects, consider positronium, a system described at long distance by a Coulomb potential with a reduced mass of \(m/2\). The analysis from section 3 follows in a nearly identical fashion, but the energy eigenvalues and quantum defects are complex, i.e.

\[
E = - \frac{q^2}{m} = \omega - \frac{\Gamma}{2},
\]

where

\[
q = \frac{m\alpha}{2n - \delta},
\]

and, at lowest order,

\[
\delta = \delta_{0,\text{re}} + i\delta_{0,\text{im}}.
\]

We will further assume that \(\delta_{0,\text{im}} \ll 1\) so that a perturbative expansion in small \(\delta\) is still possible and therefore the analysis of section 3 is equally valid; we confirm this below. From equations (56), (57), and (58), it is apparent that the real part of the energy
whereas the decay rate is given by
\begin{equation}
\Gamma = \frac{m(Z\alpha)^2}{n^3} \delta_{0,\text{im}} + ..., \tag{60}
\end{equation}
which displays the standard $n^{-3}$ dependence expected from equation (52). At higher order, $\delta_{0,\text{im}}$ could affect $\omega$ as well; however, we have already established in section 5 that this analysis is limited because it is missing relativistic corrections and therefore only these lowest-order results are worth reporting here.

Within quantum electrodynamics (QED), the lowest order decay rate of positronium is predicted to be (see, e.g., [28])
\begin{equation}
\Gamma_{\text{QED}} = \begin{cases} 
\frac{m\alpha^5}{2n^4} & \text{(singlet)} \\
\frac{4}{9\pi} (\pi^2 - 9) \frac{m\alpha^6}{2n^3} & \text{(triplet)}
\end{cases} \tag{61}
\end{equation}
which means that matching to that UV-complete theory would yield
\begin{equation}
\delta_{0,\text{im}} = \begin{cases} 
\mathcal{O}(\alpha^3) & \text{(singlet)} \\
\mathcal{O}(\alpha^3) & \text{(triplet)}
\end{cases} \tag{62}
\end{equation}

7. Discussion

We have shown how to construct a nonrelativistic effective quantum mechanics for hydrogen-like systems. The short-distance cutoff length, $r_b$ is a conceptual and calculational device used to derive our results and ultimately vanishes from any final result. The role of the boundary function is that of a coupling constant; each mode ‘feels’ a different coupling constant that varies with energy. A high energy scale, $\Lambda$ appears in the low-energy expansion of physical quantities, such as bound states. We have found non-trivial results for all angular momentum states, ultimately showing an equivalence to non-relativistic quantum defect theory. We have also shown the method provides a means of describing decays due to effects at short distance.

It was demonstrated that this approach, and therefore canonical quantum defect theory, is technically limited in applicability to purely non-relativistic systems. In future work, aspects of the non-relativistic results presented here should be applied to the relativistic, two-body version of this problem, which will allow for application to high precision atomic spectroscopy. Rydberg atoms are of particular importance because they have potential applications in quantum computing and electromagnetic field sensing, for example [29]. There also appears to be a pertinent application to positronium, in particular because of a recently discovered discrepancy between a measured transition frequency in that system and the predictions from QED [30]; this was, in fact, the subject of [27]. These ideas presumably also have applications in the areas of condensed matter, particle physics, and possibly gravitation. Like the Coulomb interaction, blackholes provide a $1/r$ potential at long distances and exhibit a kind of boundary, the event horizon, behind which information is obscured.

Data availability statement

No new data were created or analysed in this study.

Appendix. Effective description of $\ell = 2$ bound states

Here we find
\begin{equation}
\begin{align*}
\epsilon_6 = & \frac{59 - 727}{373248} - \frac{5}{20736} \frac{q}{\kappa} + \frac{(180\gamma - 197) q^2}{186624 \kappa^2} \\
& + \frac{5}{6912} \frac{q^3}{\kappa^3} + \frac{(35 - 24\gamma) q^4}{31104 \kappa^4} - \frac{1}{5184} \frac{q^5}{\kappa^5} \\
& - \frac{(4q^4 - 5q^2\kappa^2 + \kappa^4)}{10368\kappa^4} \left[ \log \frac{q}{\kappa} + \psi \left( 3 - \frac{\kappa}{q} \right) \right]. \tag{A1}
\end{align*}
\end{equation}
After expanding the digamma function in small $q/\kappa$ and writing this in terms of energies we find

$$
\epsilon_6 = \frac{\pi}{10368} \left( 1 + \frac{5E}{E_{\text{Ry}}} + \frac{4E^2}{E_{\text{Ry}}^2} \right) \cot \frac{\pi}{q} \kappa
+ \frac{59 - 72\gamma}{373248} \left( 1 + \frac{360\gamma - 283}{373248} \frac{E}{E_{\text{Ry}}} \right)
- \frac{629 - 960\gamma}{1224160} \left( \frac{E}{E_{\text{Ry}}} \right)^2 + O\left( \frac{E}{E_{\text{Ry}}} \right)^3.
$$

(A2)

We make the defect ansatz in equation (33) to find

$$
\delta = \left( 1 + \frac{5E}{E_{\text{Ry}}} + \frac{4E^2}{E_{\text{Ry}}^2} \right) \left( 1 - \frac{\pi^2}{3} \delta^2 - \frac{\pi^4}{45} \delta^4 + O(\delta^6) \right)
\times \left[ 10368\epsilon_6 - \frac{59}{36} + 2\gamma - \frac{283}{36} - 10\gamma \frac{E}{E_{\text{Ry}}} \right]
+ \left( \frac{629}{120} - 8\gamma \right) \left( \frac{E}{E_{\text{Ry}}} \right)^2 + O\left( \frac{E}{E_{\text{Ry}}} \right)^3. \tag{A3}
$$

We may parametrize the denominator of equation (A3) to be in the series form

$$
\left( 1 + \frac{5E}{E_{\text{Ry}}} + \frac{4E^2}{E_{\text{Ry}}^2} \right) \left( A_0 + A_1 \frac{E}{\Lambda} + A_2 \left( \frac{E}{\Lambda} \right)^2 + ... \right).
$$

(A4)

or, equivalently,

$$
\epsilon_6 = B_0 + B_1 \frac{E}{\Lambda} + B_2 \left( \frac{E}{\Lambda} \right)^2 + ...
$$

(A5)

where

$$
B_0 = \frac{A_0}{10368} + \frac{59}{373248} - \frac{\gamma}{5184},
$$

$$
B_1 = \frac{A_1}{10368} + \frac{283}{373248} - \frac{5\gamma}{5184} \frac{\Lambda}{E_{\text{Ry}}},
$$

$$
B_2 = \frac{A_2}{10368} + \frac{629}{1224160} - \frac{\gamma}{1296} \left( \frac{\Lambda}{E_{\text{Ry}}} \right)^2.
$$

(A6)

It follows that $\delta$ may be put in a form identical to equations (38) and (39).

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