The importance of basis states: an example using the Hydrogen basis

Lindsay Forestell and Frank Marsiglio

Department of Physics, University of Alberta,
Edmonton, Alberta, Canada, T6G 2E1

(Dated: May 14, 2015)

Abstract

We use a simple system, the electron configuration in a Hydrogen-like atom, to demonstrate the importance of using a complete basis set to provide a proper quantum mechanical description. We first start with what might be considered a successful strategy — to diagonalize a truncated Hamiltonian matrix, written in a basis consisting of Hydrogen (Z = 1) basis states. This fails to provide the correct answer, and we then demonstrate that the continuum basis states provided the rest of the true wave function, for the bound ground states. This work then shows, in a relatively simple system, the need to utilize a complete basis set, consisting of both bound and continuum states.
I. INTRODUCTION

Undergraduate texts on Quantum Mechanics generally emphasize analytical solutions to the Schrödinger Equation. But they almost always include a section on Hilbert Space, and basis states, and the formal solution of a problem through matrix mechanics. In a number of recent papers,\textsuperscript{1–3} we have illustrated, with familiar examples (Harmonic oscillator, Coulomb, etc.), the determination of bound state energies and eigenfunctions through a matrix formulation of quantum mechanics. All of these examples have used the familiar basis states which are the eigenstates for the infinite square well. In all the cases considered, we have truncated the Hilbert Space to a manageable size, so that the low-lying eigenvalues and their accompanying eigenfunctions are determined to high accuracy.

At the same time, while not really emphasized in textbooks, students are generally made aware that a proper Hilbert Space needs to complete, to be useful as a basis set. This message was driven home recently in a study of the Helium electronic ground state, utilizing a basis set consisting of two-electron product states of Hydrogenic bound state eigenfunctions.\textsuperscript{4} While this is the natural basis set to use to understand Helium (and, indeed, any multi-electron atom of the periodic table), Hutchinson et al.\textsuperscript{4} emphasized that these product states constitute an incomplete basis set, and an accurate description requires the continuum states as well. Quantum chemists learned this lesson long ago,\textsuperscript{5} and therefore never use such a (technically) poor basis set. As argued in Ref. [4], however, for state-of-the-art research problems on correlated electron systems, sometimes one does not have a choice.

The case of the Helium electronic ground state is sufficiently complicated that the lesson in Ref. [4] may be beyond the reach of undergraduates. Our purpose is to present a much simpler case, that of the one electron Hydrogen-like atom with central charge $Z_0$, which we call ‘$Z_0$Hydrogen’. Here of course the energies and states are a trivial extension to Hydrogen itself, where the Bohr radius $a_0$ is simply changed to $a_0/Z_0$.

We start first by supposing that we do not know this answer, but instead decided to formulate the problem as a matrix problem, using as a basis the familiar bound states of the Hydrogen atom. There are an infinite number of these bound states, so we must necessarily truncate. As shown in the next section the result converges very rapidly, and no more than ten or so Hydrogen bound states are required to attain a converged result, but it is the wrong result! The reason is explained, also in physical terms, and in the ensuing section we make
use of the known exact ground state for this problem to project out the contributions from each Hydrogenic state, including the continuum ones. These coefficients now sum to unity, as should be the case, for a proper description of $Z_0$ Hydrogen. We also illustrate how the continuum wave functions with increasing momentum contribute to the final (correct) wave function.

II. ATTEMPT AT A MATRIX FORMULATION FOR $Z_0$ Hydrogen

We are interested in the ground state solution for the problem of a single electron interacting with a fixed nucleus of charge $Z_0$. This has a Hamiltonian given by

$$H = -\hbar^2/2m \nabla^2 - Z_0 e^2/4\pi\epsilon_0 r,$$

where $\hbar$ is Planck’s constant, $m$ is the mass of the electron, $-e$ is the charge of the electron, $eZ_0$ is the charge of the nucleus, $\epsilon_0$ is the permittivity of free space, and $r \equiv |\vec{r}|$ is the radial coordinate. The exact eigensolutions to this problem acquire the usual three quantum numbers, $(n, \ell, m)$, and as for the case of Hydrogen, the ground state has $n = 1$ and $\ell = m = 0$, and has energy $E_1^{(Z_0)} = -Z_0^2 E_1^{(0)}$, where $E_1^{(0)} = h^2/(2ma_0^2) \equiv 13.6$ eV, and $a_0 \equiv 4\pi\epsilon_0\hbar^2/(me^2)$ is the Bohr radius. We have assumed the nucleus to be infinitely heavy so the same mass appears in Eq. (1) as appears in the definition of the Bohr radius. The exact ground state is given by

$$\psi_{100}^{(Z_0)} = 2/\sqrt{4\pi} \left(\frac{Z_0}{a_0}\right)^{3/2} e^{-Z_0r/a_0},$$

where the $1/\sqrt{4\pi}$ is the contribution from the angular part of the wave function for all s-states.

Now if we proceed as described in the Introduction, pretending not to have knowledge of this result, we would first expand the (unknown) ground state wave function in terms of a ‘handy’ set of basis states, which we denote as $\phi_i$, with the index in principle representing multiple quantum numbers. Since we are using a central potential, and we anticipate the ground state to have s-wave symmetry, then all the basis states have this symmetry as well. Thus, if we use the Hydrogen bound states as a basis set, then the label ‘$n$’ will denote the principal quantum number $n$, and $\ell = m = 0$. Writing

$$|\psi\rangle = \sum_{n=1}^{\infty} c_n |\phi_n\rangle,$$
and taking inner products with each (orthonormal) basis state and the Schrödinger Equation written in this basis results in the matrix equation

\[ \sum_{m=1}^{\infty} H_{nm} c_m = E c_m. \] (4)

This represents an infinite dimensional matrix equation, so to make progress we truncate at \( n_{\text{max}} \), vary this maximum number, and monitor the convergence of the ground state energy, for example. The required matrix elements are

\[ H_{nm} = \langle \phi_n | H | \phi_m \rangle. \] (5)

The simplest way to proceed is to rewrite the Hamiltonian, Eq. (1), as

\[ H = -\frac{\hbar^2}{2m} \nabla^2 - Z_0 \frac{e^2}{4\pi\varepsilon_0 r} \]
\[ = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi\varepsilon_0 r} \left( Z_0 - 1 \right) \frac{1}{4\pi\varepsilon_0 r} \]
\[ = H_0 + H', \] (6)

where \( H_0 \) is the actual Hamiltonian for Hydrogen (first two terms in second line) and \( H' \) is the remaining term. We begin with the diagonal terms, \( \langle \phi_n | H | \phi_n \rangle \). Because \( \phi_n \) is an eigenstate of the Hydrogen hamiltonian, these terms simplify drastically:

\[ \langle \phi_n | H_0 + H' | \phi_n \rangle = E_n + \langle \phi_n | H' | \phi_n \rangle \]
\[ = E_n - (Z_0 - 1) \frac{e^2}{4\pi\varepsilon_0} \langle \phi_n | \frac{1}{r} | \phi_n \rangle \]
\[ = -E_1^{(0)} \frac{1}{n^2} - (Z_0 - 1) \frac{e^2}{4\pi\varepsilon_0 n^2 a_0}, \] (7)

\[ = E_1^{(0)} \frac{1}{n^2} (1 - 2Z_0). \]

Here we have used the results for the energy levels of hydrogen \( (E_n = -\frac{E_1^{(0)}}{n^2}) \), and the well known result\(^6\) \( \langle \phi_n | \frac{1}{r} | \phi_n \rangle = 1/(n^2a_0) \).

Because the individual \( \phi_n \) are orthonormal eigenstates of \( H_0 \), the off-diagonal terms reduce to a simple inner product,

\[ \langle \phi_n | H_0 + H' | \phi_m \rangle = E_n \langle \phi_n | \phi_m \rangle + \langle \phi_n | H' | \phi_m \rangle \]
\[ = -(Z_0 - 1) \frac{e^2}{4\pi\varepsilon_0} \langle \phi_n | \frac{1}{r} | \phi_m \rangle \]
\[ = -2(Z_0 - 1)E_1^{(0)} \langle \phi_n | \frac{a_0}{r} | \phi_m \rangle. \] (8)
Knowing the eigenstates for Hydrogen, these integrals are individually straightforward. A general formulation requires the wavefunctions of hydrogen:

\[
\phi_{n\ell m} = \sqrt{\frac{2}{na_0^3}} \frac{(n - \ell - 1)!}{(2n)[(n + \ell)!]^3} e^{-\frac{r}{na_0}} \left( \frac{2r}{na_0} \right)^\ell L_{n-\ell-1}^{2\ell+1} \left( \frac{2r}{na_0} \right) Y_{\ell m}^m(\theta, \phi)
\]

\[
\phi_{n00} = \sqrt{\frac{2}{na_0^3}} \frac{(n - 1)!}{(2n)[(n)!]^3} e^{-\frac{r}{na_0}} L_{n-1}^1 \left( \frac{2r}{na_0} \right) \frac{1}{\sqrt{4\pi}},
\]

where in the second line \( \ell = m = 0 \). These are then substituted into the inner product in Eq. (8). The angular integral can be done immediately, as there is no angular dependence, and this eliminates the \( \frac{1}{\sqrt{4\pi}} \); furthermore, note that hereafter the letter ‘m’ denotes a principal quantum number (not the azimuthal quantum number which is now always zero):

\[
\langle \phi_m | a_0 r | \phi_n \rangle = 4 \left( \frac{m}{m+n} \right)^{\frac{1}{2}} \frac{1}{(mn)^{\frac{1}{2}} n! m!} \int_0^\infty dx x e^{-x \frac{n+m}{mn}} L_{n-1}^1 \left( \frac{2x}{n} \right) L_{m-1}^1 \left( \frac{2x}{m} \right)
\]

\[
= 4 \left( \frac{m}{m+n} \right)^{\frac{1}{2}} \frac{1}{(mn)^{\frac{1}{2}} n! m!} I_{nm},
\]

where \( I_{nm} \) is simply a number. This integral can be done numerically. Alternatively, an analytic solution to the integral is achieved by writing out the associated Laguerre polynomials as a (finite) power series.

Using this series makes the required integral elementary, so we end up with

\[
\langle \phi_m | a_0 r | \phi_n \rangle = 4 \left( \frac{m}{m+n} \right)^{\frac{1}{2}} \sum_{i=0}^{m-1} \frac{(-1)^i}{i!} \frac{(m - 1)!}{(m - 1 - i)!(i + 1)!} \left( \frac{2n}{m+n} \right)^i \sum_{j=0}^{n-1} \frac{(-1)^j}{j!} \frac{(n - 1)!}{(n - 1 - j)!(j + 1)!} \left( \frac{2m}{m+n} \right)^j (1 + i + j)!
\]

which is simply a number. Thus, the off-diagonal results for the Hamiltonian are:

\[
\langle \phi_m | H | \phi_n \rangle = -2(Z - 1)E_1^{(0)} \langle \phi_m | a_0 r | \phi_n \rangle.
\]

Following the philosophy of Ref. [1], we can simply determine the Hamiltonian matrix up to some maximum cutoff, \( n_{\text{max}} \), and diagonalize it to determine the ground state energy. The results are shown in Fig. 1. In Fig. (1a) we see that as we increase the size of the matrix for different values of \( Z_0 \), the ground state energy does converge (almost immediately). However, the energies converge to the wrong value (except the case of \( Z_0 = 1 \), which is
simply hydrogen, and obviously needs only the one basis state for the correct answer). The expected value is also indicated - it is simply \(-Z_0^2 E_1^{(0)}\), as noted previously. In Fig. (1b) we show the actual energy achieved vs. \(Z_0\), along with the exact result, and their difference. These clearly diverge, especially as \(Z_0\) increases.

\[
-\langle r \rangle \propto \frac{a_0}{Z_0}
\]

FIG. 1: (color online) (a) Ground state energy (in units of Rydbergs) for various values of \(Z_0\) as a function of matrix size. Note that in all cases convergence is achieved with \(n_{\text{max}} \approx 5\). (b) Ground state energy (in units of Rydbergs) vs. \(Z_0\) (solid blue curve) using \(n_{\text{max}} = 18\). Also shown is the exact result, \(E_0/E_1^{(0)} = -Z_0^2\) (green dashed curve) and the difference (dotted red curve). The deviation grows as \(Z_0\) increases, but notice some small discrepancies for \(Z_0 < 1\) as well. (c) An expanded view of the \(Z_0 = 0.5\) result from part (a), to better illustrate the discrepancy with the exact result. (d) An expanded view of the dependence on \(Z_0\), for \(Z_0 < 1\), showing that the difference peaks near \(Z_0 \approx 0.6\). Note that \(10 \times\) the difference is plotted to see it better.

What went wrong? As already mentioned in the Introduction, the bound state eigenstates for Hydrogen, while infinite in number, do not actually form a complete basis set. We should not have expected to get the correct result. On the other hand, truncating the Hilbert space has worked in previous studies of one and three dimensional problems.\(^1,^3\) The problem here is that as we increase \(Z_0\), we are trying to describe an atom whose electron is more tightly bound than in Hydrogen (note that \(\langle r \rangle \propto a_0/Z_0\)). But utilizing the bound excited states attempts to make use of states that are more extended, not less extended. Note that for
$Z_0 < 1$ the calculation is more accurate. However, in Fig. (1c) we show an expanded view of
the result for $Z_0 = 0.5$, and even here the matrix result disagrees with the exact result by
a small but definite amount. A closer examination of the entire low $Z_0$ region is provided
in Fig. (1d) and we see that the error has a maximum about halfway between $Z_0 = 1$ and
$Z_0 = 0$. The relative success in this region is because physically we are trying to construct
a state that is more extended compared to Hydrogen, and the excited states are helpful in
producing this. In contrast, for $Z_0 > 1$ we require the continuum states as well, as they are
perfectly capable of describing a more closely bound state (recall that an infinite set of plane
waves can describe a $\delta$-function). We demonstrate this in the next section.

It should be noted that for the sake of pedagogy a different tact could have been followed.
One could imagine wanting to solve for the ground state of $Z_0$ Hydrogen, not in terms
of the bound eigenstates of Hydrogen, but in terms of Hydrogenic states with nuclear charge
$Z_{\text{ref}}$, where the subscript ‘ref’ is short for ‘reference’. This is more artificial then the problem
already considered, but it is instructive to consider anyways, and we do so in the Appendix.

III. THE CONTRIBUTION FROM THE CONTINUUM AND A FULL SPECTRAL DECOMPOSITION

Once we recognize the need to include the continuum states in the correct description, it
immediately becomes difficult to formulate this problem as a finite-sized matrix diagonaliza-
tion problem. Here, however, we know the exact solution, so it is still possible to determine
the degree to which each basis state contributes to the overall solution; this will clearly vary
with $Z_0$. With the radial part of the wave function denoted by $R_{10}^{Z_0}(r) = \sqrt{4\pi} \psi_{100}^{Z_0}(r)$ [see Eq.
(2)], the correct spectral decomposition is given by

$$R_{10}^{Z_0}(r) = \sum_{n=1}^{\infty} a_n R_{n0}(r) + \int dpa_p R_{p0}(r), \quad (13)$$

where the $a_n$ and $a_p$ coefficients can be determined by overlap integrals (assuming the
left-hand-side is known), and these refer to the discrete ($n$) and continuum ($p$) components,
respectively. Note that in both cases symmetry considerations require only $\ell = 0$.

The procedure will be most familiar for the discrete coefficients, so we begin with these.
We take overlap integrals of Hydrogenic wave functions (with $Z = 1$) with the exact wave
function, i.e.

\[ a_n = \int_0^\infty dr \ r^2 2 \left( \frac{Z_0}{a_0} \right)^{3/2} e^{-Z_0 r/a_0} R_{n0}(r), \]  

(14)

The radial wave function \( R_{n0}(r) \) can be written in terms of an associated Laguerre polynomial, which has a known finite polynomial expansion;\(^{11}\) then the integral in Eq. (14) can be readily done, and what remains are finite sums which one can recognize as binomial expansions. The final result is

\[ a_n = \frac{8 Z_0^{3/2}}{(1 + Z_0)^3} \delta_{n,1} + (Z_0 - 1)(1 - \delta_{n,1}) \frac{8n^{3/2}Z_0^{3/2}}{(1 + nZ_0)^4} \left( \frac{nZ_0 - 1}{nZ_0 + 1} \right)^{n-2}. \]  

(15)

Note the explicit factor of \((Z_0 - 1)\) in front of the second term; for \(Z_0 = 1\), the only non-zero coefficient is the \(n = 1\) term, with coefficient unity, as must be the case. For \(Z_0 \neq 1\), all other \(s\)-states contribute with diminishing amplitude as \(n\) increases.

A numerical summation of the probabilities \(|a_n|^2\) over all values of \(n\) reveals that these do not sum to unity (when \(Z_0 \neq 1\)), i.e. a finite contribution must come from the continuum states. The continuum states for \(\ell = 0\) are denoted \(R_{p0}(r)\), where \(p\) is a continuum momentum. These eigenstates for the Hydrogen atom are less familiar to students, but they are given in standard undergraduate texts:\(^{12,13}\)

\[ R_p(r) = \frac{Z}{a_0} \sqrt{\frac{2\pi pa_0}{Z}} e^{-ipr} M(1 + i \frac{Z}{pa_0}, 2, 2ipr), \]  

(16)

where we have written this for general \(Z\) but require only \(Z = 1\), and

\[ M(a, b, z) \equiv \sum_{m=0}^{\infty} \frac{(a)_m z^m}{(b)_m m!} \]  

(17)

is the so-called Kummer function,\(^{14,15}\) and \((a)_m \equiv a(a+1)(a+2)\ldots(a+m-1)\) is the so-called Pochhammer symbol. Note that \((a)_0 \equiv 1\), and \((2)_m = (m+1)!\), for example. Equation (16) is a general solution, and is connected to the Laguerre polynomials that describe the radial bound state wave functions.\(^{16}\)

The standard\(^{12}\) normalization condition for the continuum states,

\[ \int_0^\infty dr \ r^2 R_{p'}(r) R_p(r) = \delta(p' - p), \]  

(18)

determines the coefficient in Eq. (16). By utilizing the expansion in Eq. (17) we can evaluate the overlap integral required to obtain the coefficient \(a_p\), for \(Z = 1\),

\[ a_p = \frac{4}{\sqrt{a_0}} \frac{(Z_0a_0)^{3/2}(Z_0 - 1)}{[(pa_0)^2 + Z_0^2]^2} \sqrt{\frac{2\pi pa_0}{1 - e^{-2\pi pa_0}}} \exp \left[ -\frac{2}{pa_0} \tan^{-1} \left( \frac{pa_0}{Z_0} \right) \right]. \]  

(19)
These coefficients, when squared, show a distribution peaked around $p \approx Z_0/a_0$, as expected. Since these enter linearly in the wave function expansion given in Eq. (13), we show in Fig. (2) the amplitudes, $a_p/a_0$ vs. $pa_0$ for a variety of values of $Z_0$, showing how contributions from the continuum peak near $pa_0 \approx Z_0$. The larger $Z_0$, the larger is the contribution from the continuum states.

To sum the continuum contributions one requires a factor of $2/\pi$ to account for the enumeration of continuum states; then the contribution from the all the continuum states is

$$ P_{\text{cont}} = \frac{2}{\pi} \frac{32\pi (Z_0 - 1)^2}{Z_0^3} \int_0^\infty dy \frac{y}{(y^2 + 1)^4} \frac{1}{1 - e^{-2yZ_0}} \exp \left( -\frac{4}{yZ_0} \tan^{-1} y \right). $$

The contributions from the various states to the ground state are displayed in Fig. (3). We have checked that for all $Z_0$ the contributions sum to unity. Note that for $Z_0 > 1$ the continuum states play an increasingly important role. Let us repeat the reason, now that we Fig. (3). In this regime the actual wave function, given by Eq. (2), varies on a scale of $a_0/Z_0$. For $Z_0 > 1$ none of the bound states can provide structure on such a scale; as $n$ increases the
FIG. 3: (color online) Various contributions from the Hydrogenic bound and continuum states to the ground state wave function for a central charge with magnitude $eZ_0$, as a function of $Z_0$. At $Z_0 = 1$ only the $1s$ state contributes, as expected. For $Z_0 \neq 0$ all other states contribute as well. In particular, for $Z_0 > 1$ the continuum states contribute with increasing amplitude for reasons explained in the text. The sum of the three curves is unity for all $Z_0$, as indicated by the thick horizontal (purple) line across the top.

Hydrogenic basis states become more extended, not less. The only source of variation on this scale is the spectrum of continuum states, and these are readily utilized.

The degree to which different continuum momentum eigenstates contribute is illustrated in Fig. (4), where we show the wave function given by Eq. (13) for a particular example, $Z_0 = 1.5$, but with the momentum integration cut off at increasing values of momentum. As compared with the exact wave function it is clear that initial components (near $pa_0 \approx 0$) first fix the large $r$ behavior (the bound states produced a value that was too high for $r/a_0 \approx 1$) and components with larger value of momentum then begin to produce larger amplitude near the origin. This figure demonstrates explicitly what we were just explaining, that finer scale contributions were necessarily produced by the continuum states.

This example serves to show how a ‘poor’ basis choice (i.e. using the Hydrogenic set for $Z = 1$ rather than for $Z = Z_0$) can require the use of the continuum states. For the case of a
FIG. 4: (color online) The evolution of the ground state wave function from just considering the bound states, i.e. the lowest (blue) curve to the exact result (blue squares). As the accuracy increases we cut off the momentum integration in Eq. (13) at $p_c a_0 = 1$ (next highest (red) curve), $p_c a_0 = 3$ (next highest (green) curve), $p_c a_0 = 10$ (next highest (black) curve), and finally, $p_c a_0 = 50$ (next highest (red) curve). The higher momentum continuum components contribute to the wave function near the origin.

A single electron bound to a positive charge, a ‘poor’ choice can obviously be avoided. However, in the case of many electron problems where locally one can have either a single electron or two electrons, it is very difficult to devise a basis set that diagonalizes both scenarios.\(^4\)

**IV. SUMMARY**

We have used one of the simplest yet realistic quantum systems, the electron configuration in a Hydrogen-like atom, to demonstrate a principle with which most students are familiar, but likely few have encountered in practice: the need for a complete basis set to describe properly a quantum mechanical system. The Hydrogen-like atom serves as a good system to show this, since we know the exact solution, and hence know in advance the correct answers. We can also do most of the required integrals, both for the matrix formulation, and for the
spectral decomposition. The matrix formulation did not work, perhaps counter to what some might expect. The implication of this failure, that continuum states are necessary, was reinforced by carrying out a spectral decomposition. This result, portrayed in Fig. (3), perhaps runs counter to our intuition, that bound states require a partial amplitude (that can be substantial!) corresponding to continuum states, i.e. states in which the particle is free to roam through all space. We also provided a physical understanding of why these states were especially required when we attempt to construct states that are more tightly bound than provided by the bound basis functions, as demonstrated explicitly in Fig. (4).

Acknowledgments

We thank Don Page and Bob Teshima for helpful discussions concerning the treatment of the continuum states. This work was supported in part by the Natural Sciences and Engineering Research Council of Canada (NSERC), by the Alberta iCiNano program, and by a University of Alberta Teaching and Learning Enhancement Fund (TLEF) grant.

Appendix A: A Matrix formulation using $Z_{\text{ref}} \neq 1$

As in Section [II] we wish to solve for the Hamiltonian

$$H = -\frac{\hbar^2}{2m} \nabla^2 - Z_0 \frac{e^2}{4\pi \epsilon_0} \frac{1}{r},$$

but we now rewrite this using a slightly different decomposition:

$$H = -\frac{\hbar^2}{2m} \nabla^2 - \frac{e^2}{4\pi \epsilon_0} \frac{Z_{\text{ref}}}{r} + (Z_{\text{ref}} - Z_0) \frac{e^2}{4\pi \epsilon_0} \frac{1}{r}$$

$$= H_0 + H'.$$

The motivation is that we need more tightly bound wave functions to describe ultimately the ground state for $Z_0\text{Hydrogen}$. But if $Z_{\text{ref}} >> Z_0$ then many of the bound states will actually be more ‘compact’ compared to the ground state we are seeking to find. Therefore, proceeding as before, we begin with the diagonal terms, $\langle \phi_n | H | \phi_n \rangle$, to obtain

$$\langle \phi_n | H_0 + H' | \phi_n \rangle = E_n + \langle \phi_n | H' | \phi_n \rangle$$

$$= E_n + (Z_{\text{ref}} - Z_0) \frac{e^2}{4\pi \epsilon_0} \langle \phi_n | \frac{1}{r} | \phi_n \rangle$$

$$= -Z_{\text{ref}}^2 \frac{E_1^{(0)}}{n^2} + (Z_{\text{ref}} - Z_0) \frac{e^2}{4\pi \epsilon_0} \frac{Z_{\text{ref}}}{n^2 a_0}.$$
Here we have used the results for the energy levels of a hydrogenic state with nuclear charge $Z_{\text{ref}}$: $E_n = -Z_{\text{ref}}^2 \frac{E_1^{(0)}}{n^2}$, and the generalization of the well known result$^6$ $\langle \phi_n | \frac{1}{r} | \phi_n \rangle = Z_{\text{ref}}/(n^2a_0)$.

\[ \langle \phi_m | H | \phi_n \rangle = 2E_1^{(0)} Z_{\text{ref}} (Z_{\text{ref}} - Z_0) J_{nm}, \] 

where

\[ J_{nm} \equiv 4 \frac{(mn)^{\frac{1}{2}}}{(m+n)^2} \sum_{i=0}^{m-1} \frac{(-1)^i}{i!} \frac{(m-1)!}{(m-1-i)!(i+1)!} \left( \frac{2n}{m+n} \right)^i \]

\[ \sum_{j=0}^{n-1} \frac{(-1)^j}{j!} \frac{(n-1)!}{(n-1-j)!(j+1)!} \left( \frac{2m}{m+n} \right)^j (1+i+j)! \] 

\[ (A4) \]

is the same number given by Eq. (10) in Section II.

Now we can simply diagonalize an $N \times N$ matrix for some $Z_{\text{ref}}$. In Fig. (5) we show the ground state energy obtained in this way for a targeted system with $Z_0 = 3$. Use of the usual Hydrogen states with $Z_{\text{ref}} = 1$ produces a very poor result, $E_0 \approx -5E_1^{(0)}$, compared to the

FIG. 5: (color online) The ground state energy for a $Z_0$ Hydrogen system with $Z_0 = 3$, vs. $Z_{\text{ref}}$. This calculation was performed by diagonalizing a $18 \times 18$ matrix, and shows that using larger values of $Z_{\text{ref}}$ is effective to a degree. Results are definitely more accurate than using $Z_{\text{ref}} = 1$ for example, but the convergence to very accurate results is very slow.
exact result, \( E_{0}^{\text{ex}} = -9 E_{1}^{(0)} \). As we increase \( Z_{\text{ref}} \) the result becomes more accurate, and of course exact as \( Z_{\text{ref}} \to Z_0 \). For larger values of \( Z_{\text{ref}} \) the result first deteriorates before steadily improving as \( Z_{\text{ref}} \) continues to increase towards 100, as shown. While the convergence is quite slow, nonetheless this exercise demonstrates that using large values of \( Z_{\text{ref}} \) allows one to get reasonably accurate results for the reason that the bound state basis set now contains quite a number of wave functions that describe a particle confined to the origin. Nonetheless, the lack of better accuracy is an indication that a continuous set of continuum states in the end offers more flexibility than a discrete set of bound states. Note that we did not require values of \( N \) in excess of about 20 to achieve converged results for all values of \( Z_{\text{ref}} \) shown.

[1] F. Marsiglio, “The harmonic oscillator in quantum mechanics: a third way,” Am. J. Phys. 77, 253 (2009).
[2] V. Jelic and F. Marsiglio, “The double-well potential in quantum mechanics: a simple, numerically exact formulation,” Eur. J. Phys. 33 1651-1666 (2012).
[3] B.A. Jugdutt and F. Marsiglio, “Solving for three-dimensional central potentials using numerical matrix methods,” Am. J. Phys. 81 343-350 (2013).
[4] Joel Hutchinson, Marc Baker and Frank Marsiglio, “The spectral decomposition of the helium atom two-electron configuration in terms of hydrogen orbitals,” Eur. J. Phys. 34 111-128 (2013). See also H.O. Di Rocco, “Comment on 'The spectral decomposition of the helium atom two-electron configuration in terms of hydrogenic orbitals,' ” Eur. J. Phys. 34, L43-L45 (2013), where the need for the continuum states is reinforced through their requirement to obtain correct results for various sum rules.
[5] See E.A. Hylleraas, “On the Ground State of the Helium Atom,” Z. Phys. 48, 469 (1929). In this paper (which precedes the paper below, Hylleraas alludes to calculations by a Dr. Biemüller, which apparently failed for exactly the same reason ours will not fully succeed — because the discrete states exemplified by Eq. (9) do not form a complete set, and the continuum states are required as well. The paper which describes the famous Hylleraas variational states is E.A. Hylleraas, “A New Calculation of the Energy of Helium in the Ground State as Well as the Lowest Term of Ortho-helium,” Z. Phys. 54, 347 (1929). Both these papers are reprinted in English in Quantum Chemistry: Classic Scientific Papers, by H. Hettema (World Scientific,
Singapore, 2000). See also *Mathematical and Theoretical Physics, Volume II*, by E.A. Hylleraas (Wiley-Interscience, Toronto, 1970), particularly Chapter 7.

[6] D. J. Griffiths, *Introduction to Quantum Mechanics* (Pearson/Prentice Hall, Upper Saddle River, NJ, 2005), 2nd edition.

[7] Ira N. Levine, *Quantum Chemistry*, 6th Edition (Pearson, Upper Saddle River, 2009).

[8] See, for example, Eqs. (6-8) in Ref. [1].

[9] See Ref. [6], and note that the Laguerre polynomials are defined in this reference in a manner that often differs from alternate definitions by a factorial factor. For example, $L^{2\ell+1}_{n-\ell-1}$, so, for us, $L^1_{n-1} = \frac{1}{n!}L^1_{n-1}$, where $L^1_{n-1}$ denotes the notation used by Griffiths and $L^1_{n-1}$ denotes the notation used by Arfken, in G. Arfken, *Mathematical Methods for Physicists, Third Edition*, (Academic Press, Toronto, 1985).

[10] Remarkably, this integral was first solved in E. Schrödinger, “Quantisation as a Problem of Proper Values (Part III)”, Annalen der Physik 80, (1926). See *Collected Papers on Wave Mechanics*, (Blackie and Son Limited, London, 1928) pp. 62-101 for an English translation.

[11] For definiteness we write out the definition of the associated Laguerre polynomials that we use in this paper, following Ref. [6] as a closed form sum:

$$L^k_n(x) = (n+k)! \sum_{j=0}^{n} \frac{(n+k)!}{(n-j)!(k+j)!} \frac{(-x)^j}{j!}.$$  \hspace{1cm} (A6)

Note the additional factor of $(n+k)!$ — see Ref. [9].

[12] L.D. Landau and E.M. Lifshitz, *Quantum Mechanics*, 2nd Edition, (Pergamon Press, New York, 1965). See in particular Section 36, and Eq. (33.4) for the normalization condition.

[13] E. Merzbacher, *Quantum Mechanics*, 3rd Edition, (John Wiley and Sons, Inc., Hoboken, 1998).

[14] M. Abramowitz and I.A. Stegun, *Handbook of Mathematical Functions with Formulas, Graphs, and Mathematical Tables* (Dover Publications, Inc. New York, 1972).

[15] Frank W.J. Olver, Daniel W. Lozier, Ronald F. Boisvert, and Charles W. Clark, *NIST Handbook of Mathematical Functions*, (Cambridge University Press, Cambridge, 2010).

[16] In fact

$$L^k_n(x) = \frac{(k+1)_n}{n!} M(-n,k+1,x) = \frac{(n+k)!}{k!n!} M(-n,k+1,x),$$  \hspace{1cm} (A7)

and it should be clear that this equation is consistent with Eq. (A6) in Ref. [11] and Eq. (17) in the text.