Spectroscopy of Antihydrogen in a Laser Field via the Time-Dependent Schrödinger Equation

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Abstract

We present a method for numerically solving the Schrödinger equation of an antihydrogen atom in a laser field. This method involves discrete variable representation (DVR), quintic spline approximation of the radial part of the wavefunction, and Gaussian quadrature on the angular and radial variables. We include a description of the computer program that was created to perform calculations of transition probabilities, and present data from simple test case in which the atom is initially in the $3s$ state.

Contents

1 Introduction

Since this is a senior thesis, written mainly for myself, the audience is assumed to be students at my own current level who have already taken a course on quantum mechanics but who have not necessarily dealt with numerical solution of the time dependent Schrödinger equation. Even with such an audience, the results of this research are new and of interest to professional physicists. Experimentalists are trying to explore the nature of antimatter by examining antihydrogen, the first and only antimatter atom that has been created so far. Our results should help shed a little light on the topic so that they are not wandering about in the dark. It should give them useful information in their pursuit of methods to prepare antihydrogen atoms for the spectroscopic experiments that will help reveal the nature of antimatter.

The creativity and labor of the research originates with Dr. Chi-Yu Hu, my advisor, and David Caballero, her graduate student. They have selected the mathematical and computational techniques described in this paper and have written the computer code to calculate the results. I have only created this expository paper, run the code, and included the results of the research within. The final results of their research will be communicated to the professional physics community once they themselves write a paper.

A number of appendices are included at the end of this paper to aid the reader (and the author) in comprehending various aspects of this paper. Since the reader is likely to be relatively new to the topic of quantum mechanics, Appendix A covers derivation of the solutions for the ordinary hydrogen-in-free-space problem. These solutions are very important to our antihydrogen problem, assuming that nature provides the expected symmetry that would give the hydrogen and antihydrogen systems identical behavior. Appendix B gives explicit equations for the functions which are used in the spline approximation of the antihydrogen wavefunction. Finally, Appendix C provides a short description of the basics of antimatter for those unfamiliar with its relation to matter. Now, let's get to the problem in question.

1.1 Physical Situation

Imagine, if you will, that we have an antihydrogen atom free in space that is excited at some quantum state with a principal quantum number[1] $n \approx 50$. In actuality, experimental physicists create antihydrogen atoms in the strong electromagnetic fields that are used to trap antiprotons and positrons, so they are not free, but we theorists will assume for now that our atom is essentially free. The atom remains in its excited state until we turn on a laser beam designated to be linearly polarized along the z-axis. Then the atom remains in a laser field of particular frequency ν_L and intensity I for some length of time. This is, theoretically, our physical situation.

1.2 Objective

What we would like to do is calculate the probabilities of excitation and de-excitation (including ionization) of the atom due to the laser beam as time goes on, given various particular combinations of frequency and intensity of the beam. We are especially interested

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[1] See Appendix A for the derivation of the principal quantum number n and the corresponding states.

in de-excitation because experimental physicists would like to know how to bring their antihydrogen atoms (which have $n \approx 50$) to lower energy, or "cooler," states. That would allow them to perform spectroscopic experiments with the atoms that could help reveal the nature of antimatter. We will be looking specifically at the probabilities of the antihydrogen atom occupying states of particular principal and angular quantum numbers, that is, particular R_{nl} states.

1.3 Procedure

We calculate the wavepacket as a function of time using a program written by David Caballero in the C programming language. From this wavefunction, the probabilities of ionization and transition to particular bound antihydrogen states can be calculated. To explain this procedure in a cogent manner, this paper is organized into three main sections. "Mathematical Work" presents the mathematics and technique leading up to the program, "Computational Work" provides a description of the program and the resulting data, and "Conclusions" presents the physical implications of the data.

2 Mathematical Work

First, in "Analytical Approach," we examine the progress we can make analytically towards the solution. However, it is a very rare circumstance that one can solve a quantum mechanical problem analytically, such as in the case of the quantum simple harmonic oscillator or the free hydrogen atom. So, once we reach a point where we can push the analysis no further, we take a discrete variable approach to find a method for computing an approximate solution. We find in "Discrete Variable Approach" that it is useful to work in both momentum- and coordinate-space representations and that using a quadrature technique on the angular coordinates and a spline technique on the radial coordinates is to our advantage.

2.1 Analytical Approach

To achieve our goal of calculating probabilities of excitation and de-excitation to particular states, we need to solve the time-dependent Schrödinger equation for the wavefunction $\Psi(\mathbf{r},t)$ of the atom[2]. Given our knowledge of the initial state $\Psi(\mathbf{r},0)$, we should be able to discover how the wavefunction evolves over time as a wavepacket of states, with the most appropriate basis being the free-hydrogen bound states ψ_{nlm}, with negative energy, and ionized continuum states[3] ψ_E, with positive energy. With respect to this basis,

$$\Psi(\mathbf{r},t) = \sum_{nlm} A_{nlm}(t)\,\psi_{nlm}(\mathbf{r}) + \int_0^\infty A_E(t)\,\psi_E(\mathbf{r})\,dE, \tag{2.1}$$

where A_{nlm} and A_E are the complex probability amplitudes of the packet components and the triple sum over n, l, and m is expressed compactly using only one summation symbol. The continuum states are infinitely degenerate, meaning there are infinitely many continuum states with the same energy levels, so the unbound component of Ψ is much more complicated than the integral in Equation 2.1 suggests. Since we do not know how to characterize the continuum states, we will not try to extract information about energy from these states. On the other hand, the value of n determines the energy E_n associated with the bound state ψ_{nlm}, so we have access to the probability of the atom taking on bound states with particular values of n. For each value of n, there are n^2 states with different l and m values, so we should consider each of them in our calculation. Using Equation 2.1 and the orthonormality of the bound states, the probability $P_n(t)$ that the antihydrogen atom will be in a state with energy E_n at time t is

$$\begin{aligned} P_n(t) &= \left|\left\langle \sum_{lm} \psi_{nlm}(\mathbf{r}) \middle| \Psi(\mathbf{r},t) \right\rangle\right|^2 = \left| \sum_{lm} \langle \psi_{nlm}(\mathbf{r}) | \Psi(\mathbf{r},t) \rangle \right|^2 \\ &= \left| \sum_{lm} \left\langle \psi_{nlm}(\mathbf{r}) \middle| \sum_{n'l'm'} A_{n'l'm'}(t)\,\psi_{n'l'm'}(\mathbf{r}) \right\rangle \right|^2 \end{aligned}$$

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[2] As we do in Appendix A with the hydrogen atom, we use the center-of-mass reference frame, so the wavefunction approximately discribes the positron. We also assume that the atom is not moving at a relativitic velocity, and (anything else? about the electromagnetic field? spin?).

[3] The continuum states are essentially all states outside of the span of the bound states.

$$= \left| \sum_{lm} \sum_{n'l'm'} A_{n'l'm'}(t) \left\langle \psi_{nlm}(\mathbf{r}) | \psi_{n'l'm'}(\mathbf{r}) \right\rangle \right|^2 = \left| \sum_{lm} A_{nlm}(t) \right|^2 . \tag{2.2}$$

More specifically, the probability that antihydrogen atom occupies a state with particular values of n and l at time t is

$$P_{nl}(t) = \left| \sum_{m} A_{nlm}(t) \right|^2 . \tag{2.3}$$

The probability that the atom is ionized $P_i(t)$ at time t is simply the probability that the positron does not take any bound state at time t:

$$P_i(t) = 1 - \sum_{n} P_n(t). \tag{2.4}$$

These ionization and transition probabilities are precisely what we are after.

Returning to the issue of the Schrödinger equation, we must apply our knowledge of the physical situation to determine the form of the Hamiltonian operator $\hat{H}(\mathbf{r}, t)$. The equation is as follows:

$$i\hbar\dot{\Psi}(\mathbf{r}, t) = \hat{H}(\mathbf{r}, t)\Psi(\mathbf{r}, t), \tag{2.5}$$

where

$$\hat{H}(\mathbf{r}, t) = \hat{H}_0(\mathbf{r}) + \hat{h}(\mathbf{r}, t), \tag{2.6}$$

with $\hat{H}_0(\mathbf{r})$ representing the Hamiltonian of the positron about the antiproton and $\hat{h}(\mathbf{r}, t)$ representing the positron's interaction with the external laser field. In analogy to the case of the regular hydrogen atom, we can deduce this:

$$\hat{H}_0(\mathbf{r}) = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{\mu r}\frac{\partial}{\partial r} + \frac{\hat{L}^2}{2\mu r^2} - \kappa\frac{e^2}{r}, \tag{2.7}$$

where $\hat{L}$ is the angular momentum operator, μ is the reduced mass of the two-particle system, and κ is Coulomb's constant. For the laser field, which will be approximated as an electromagnetic plane wave (linearly (is this pertinent?)) polarized along the z-axis and travelling in the x-direction, we know this:

$$\hat{h}(\mathbf{r}, t) = Er\cos\theta\sin\omega t, \tag{2.8}$$

where E is the magnitude of the electric component of the laser field with intensity $I = \sqrt{\varepsilon_0/\mu_0}E^2$ and ω is the angular frequency, given the laser's frequency $\nu_L = (kc/2\pi) = \omega/2\pi$. Of course, ε_0 is the permittivity of free space, μ_0 is the permeability of free space, and c is the speed of light. So, Schrödinger's equation for this situation is

$$i\hbar\dot{\Psi}(\mathbf{r}, t) = \left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{\mu r}\frac{\partial}{\partial r} + \frac{\hat{L}^2}{2\mu r^2} - \kappa\frac{e^2}{r} + Er\cos\theta\sin\omega t \right] \Psi(\mathbf{r}, t). \tag{2.9}$$

We want to solve this equation, but since it has been proven to be impossible to solve analytically (by whom? when?), we are forced to move to discrete-variable, numerical methods to find approximate solutions.

2.2 Discrete Variable Approach

Since we ran into difficulty (i.e. impossibility) with the analytical approach, we move on to a discrete variable approach, toward approximate relations. It is quite natural to start by discretizing the time variable, so that is the topic of the first subsection. In the subsequent subsection we discuss angular momentum- and coordinate-space representations of the operators and wavefunctions and we move into matrix and vector notation. After that, we discretize the angular variables and explain our angular quadrature technique. Finally, in the last subsection we discretize the radial coordinates and describe the spline technique and radial quadrature rule.

2.2.1 Discrete Time

When we decide to "go discrete," one possible first step is to consider an alternative form of the Schrödinger equation – the propagator form:

$$\Psi(\mathbf{r},t) = e^{-i\hat{H}(\mathbf{r},0)\,t/\hbar}\Psi(\mathbf{r},0), \tag{2.10}$$

or

$$\Psi(\mathbf{r},t+\Delta t) = e^{-i\hat{H}(\mathbf{r},t)\,\Delta t/\hbar}\Psi(\mathbf{r},t), \tag{2.11}$$

where the exponential part of the equation "propagates" the wavefunction through time and is thus called the time propagator. Expanding the propagator out to its polynomial form gives us the meaning of the Equation 2.11:

$$\Psi(\mathbf{r},t+\Delta t) = \left[1 - i\frac{\Delta t}{\hbar}\hat{H} - \frac{1}{2}\left(\frac{\Delta t}{\hbar}\right)^2\hat{H}^2 + i\frac{1}{6}\left(\frac{\Delta t}{\hbar}\right)^3\hat{H}^3 + \cdots\right]\Psi(\mathbf{r},t), \tag{2.12}$$

where $\hat{H}$ is evaluated at position $\mathbf{r}$ and time t. If Δt is infinitessimally small, this leads us straight back to the original form of the Schrödinger equation: when $(\Delta t)^2$ is negligible, we have

$$\Psi(\mathbf{r},t+\Delta t) \approx \Psi(\mathbf{r},t) - i\frac{\Delta t}{\hbar}\hat{H}(\mathbf{r},t)\,\Psi(\mathbf{r},t), \tag{2.13}$$

or

$$\frac{\Psi(\mathbf{r},t+\Delta t) - \Psi(\mathbf{r},t)}{\Delta t} \approx -\frac{i}{\hbar}\hat{H}(\mathbf{r},t)\Psi(\mathbf{r},t), \tag{2.14}$$

and taking the limit of this equation (or Equation 2.12) as Δt goes to zero yields the familiar form.

So, then, we're dealing with the propagator form of Schrödinger's equation with finite Δt. That implies that we could easily discretize time and talk about moments in time t_k that are separated by the interval Δt rather than continuous time t. Thus, starting with the initial state where $t = t_0 = 0$, each application the time propagator will advance the approximate solution wavefunction in time by Δt from t_k to $t_{k+1} = t_k + \Delta t$:

$$\Psi(\mathbf{r},t_{k+1}) = \left[1 - i\frac{\Delta t}{\hbar}\hat{H} - \frac{1}{2}\left(\frac{\Delta t}{\hbar}\right)^2\hat{H}^2 + i\frac{1}{6}\left(\frac{\Delta t}{\hbar}\right)^3\hat{H}^3 + \cdots\right]\Psi(\mathbf{r},t_k), \tag{2.15}$$

where $\hat{H}$ is evaluated at position $\mathbf{r}$ and time t_k. Remembering that $\hat{H}$ here is the big operator we saw in brackets in the original form of Schrödinger's equation (Equation 2.9), this looks a lot messier than what we started with. If we didn't have any tricks up our sleeve, we'd cut this polynomial off, probably at the second term, necessitating that $(\Delta t)^2$ be negligible.

But here's where we reach up our sleeve. Following a procedure suggested by G. I. Marchuk [1], we replace the propagator with this:

$$\left[\left(1+i\frac{\Delta t}{2\hbar}\hat{h}\right)^{-1}\left(1-i\frac{\Delta t}{2\hbar}\hat{h}\right)\left(1+i\frac{\Delta t}{2\hbar}\hat{H}_0\right)^{-1}\left(1-i\frac{\Delta t}{2\hbar}\hat{H}_0\right)\right]. \tag{2.16}$$

Note that this expression *is* a product of operators, where no operator contains both $\hat{h}$ and $\hat{H}_0$. We can make this replacement because if we expand the given expression (by using a binomial expansion to take care of the exponents and multiplying the terms out) and collect terms with like powers of Δt, then we find that it matches the true propagator up to terms of order $(\Delta t)^2$:

$$\begin{aligned}\Bigg[1 - i\frac{\Delta t}{\hbar}\left(\hat{H}_0+\hat{h}\right) - \frac{1}{2}\left(\frac{\Delta t}{\hbar}\right)^2\left(\hat{H}_0+\hat{h}\right)^2 \\ + i\frac{1}{6}\left(\frac{\Delta t}{\hbar}\right)^3\left(\frac{3}{2}\hat{H}_0{}^3+3\hat{H}_0{}^2\hat{h}+3\hat{H}_0\hat{h}^2+\frac{3}{2}\hat{h}^3\right) + \cdots\Bigg].\end{aligned} \tag{2.17}$$

The price for using this operator, then, is that we'll have to keep $(\Delta t)^3$ negligible when we do our calculations, so that our new replacement-propagator equation holds approximately true. Well, that's cheaper than the cost of our default technique, where we had to keep $(\Delta t)^2$ negligible. This replacement is sounding good already, but wait, there's more!

If we break the operator in half and rearrange the equation slightly, we'll find that we have a very simple set of resulting operators on our hands. We can consider the operator in Expression 2.16 as four operators multiplied together, where each operator acts in succession on the wavefunction. Breaking the quartet of operators in half, we can consider the right two to be acting first and the left two to be acting second. So after applying the first set of operators, we get an intermediate wavefunction between $\Psi(\mathbf{r}, t_k)$ and $\Psi(\mathbf{r}, t_{k+1})$, and then applying the second set of operators gives us $\Psi(\mathbf{r}, t_{k+1})$. We might as well call the intermediate wavefunction $\Psi(\mathbf{r}, t_{k+1/2})$ to keep track of our progress toward the solution; whether or not this wavefunction actually approximates the solution function at $t = t_{k+1/2} = t_k + \frac{\Delta t}{2}$ is not our concern because we will not keep this information in the final solution. Now we can write the two steps out as

$$\Psi\left(\mathbf{r}, t_{k+1/2}\right) = \left[\left(1+i\frac{\Delta t}{2\hbar}\hat{H}_0\right)^{-1}\left(1-i\frac{\Delta t}{2\hbar}\hat{H}_0\right)\right]\Psi(\mathbf{r}, t_k) \tag{2.18}$$

and

$$\Psi(\mathbf{r}, t_{k+1}) = \left[\left(1+i\frac{\Delta t}{2\hbar}\hat{h}\right)^{-1}\left(1-i\frac{\Delta t}{2\hbar}\hat{h}\right)\right]\Psi(\mathbf{r}, t_{k+1/2}). \tag{2.19}$$

Rearranging these equations gives us

$$\left(1 + i\frac{\Delta t}{2\hbar}\hat{H}_0\right)\Psi(\mathbf{r}, t_{k+1/2}) = \left(1 - i\frac{\Delta t}{2\hbar}\hat{H}_0\right)\Psi(\mathbf{r}, t_k) \tag{2.20}$$

and

$$\left(1 + i\frac{\Delta t}{2\hbar}\hat{h}\right)\Psi(\mathbf{r}, t_{k+1}) = \left(1 - i\frac{\Delta t}{2\hbar}\hat{h}\right)\Psi(\mathbf{r}, t_{k+1/2}). \tag{2.21}$$

These two resulting equations and their operators are simple because each find simple expression once put in the appropriate representation. The first equation uses $\hat{H}_0$ exclusively, which, in matrix form, is diagonalizable in its angular momentum representation because it includes $\hat{L}^2$. The second equation uses $\hat{h}$ exclusively, which is diagonalizable in its (spherical) coordinate representation. If each part of the operator were kept together, the matrix form of the operator would have off-diagonal entries in either representation. Also, we prefer the arrangement of Equations 2.20 and 2.21 to that of Equations 2.18 and 2.19 because it is easier to solve a matrix equation of the form $A\mathbf{x}=\mathbf{b}$ by Gauss-Jordan elimination of the augmented matrix $[A\,\mathbf{b}]$ than to find the inverse of A and multiply $\mathbf{b}$ by it. It would be prudent now to discuss the intricacies of these representations and the matter of transformation between the representations.

2.2.2 Angular Momentum- and Coordinate-Space Representations

Now that we know we would like to work with the wavefunction in a momentum basis, we propose that we can express the solution wavefunction in terms of the angular momentum operator's eigenfunctions. We know that the spherical harmonics Y_{lm} are eigenfunctions of $\hat{L}$ with eigenvalues determined by the quantum number l, but they are also eigenfunctions for $\hat{L}_z$, the polar component of $\hat{L}$, with eigenvalues determined by m. All we want, though, is a basis of eigenstates for $\hat{L}^2$, that is, a basis where each element has a particular l-value. So we may add spherical harmonics with the same l-value and different m-values to produce the most general form of basis that we desire. Given a particular value for l, there are $2l+1$ spherical harmonic basis functions, and since our new basis must span the same space, it must have the same number of independent functions. We'll use the index p to distinguish these $2l+1$ functions and let p range from 0 to $2l$.[4] Additionally, we will use an index ν to represent a particular combination of l and p, so $\nu \equiv (l_\nu, p_\nu)$.[5] Thus, we form a basis of angular momentum eigenstates Υ_ν of the form

$$\Upsilon_\nu(\Omega) = \Upsilon_{lp}(\Omega) = \sum_m O_{pm}\, Y_{lm}(\Omega), \tag{2.22}$$

where the sum runs over all values of m given a particular value of l. Furthermore, since we would like this basis to be orthonormal as our original basis was, we constrain the complex

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[4] Later, when we choose a finite number of momentum states for an approximate basis, there will not necessarily be $2l+1$ functions per l-value, so the range of p may be smaller than from 0 to $2l$ for some l-values.

[5] There are countably infinitely many of these combinations, so ν may be any integer from one to infinity. Also, we will oftentimes use the simplified relation $\nu = (l, p)$, where the subscripts are understood, to keep things clean.

coefficients O_{pm} such that

$$\int \Upsilon_\nu^*(\Omega)\, \Upsilon_{\nu'}(\Omega)\, d\Omega = \delta_{\nu\nu'}, \tag{2.23}$$

which means

$$\sum_m O_{pm}^*\, O_{p'm} = \delta_{pp'}. \tag{2.24}$$

Now that we have defined the basis for the momentum-space representation, our proposal that we may express Ψ in this representation may be stated mathematically:

$$\Psi(r, t, \Omega) = \sum_\nu F_\nu(r, t)\, \Upsilon_\nu(\Omega), \tag{2.25}$$

where F_ν is a complex function on the non-negatives r and t that is associated with a particular basis element Υ_ν, and the sum runs over all possible values of ν. Note that this claim is being made in addition to our first claim in Equation 2.1 that the wavefunction has a bound and an ionized component.

Equation 2.25 expresses the wavefunction Ψ in its (angular) momentum-space representation, but we can use vector notation to denote this representation more compactly. Defining $\Psi^M(r, t)$ to be the momentum-space representation of $\Psi(r, t, \Omega)$, we have

$$\Psi^M(r, t) = \begin{bmatrix} F_1(r, t) \\ F_2(r, t) \\ F_3(r, t) \\ \vdots \end{bmatrix}, \tag{2.26}$$

where there is a countably infinite number of components in the vector, with each component corresponding to a particular angular momentum basis element Υ_ν. The νth component in the vector Ψ^M may be expressed as $\Psi^M_\nu = F_\nu$.

So far we've described the wavefunction in the momentum-space representation, but we haven't yet mentioned the operators in question. If we look again at Equation 2.20 and express the wavefunction in our new representation, then we have

$$\left(1 + i\frac{\Delta t}{2\hbar}\hat{H}_0(r, \Omega)\right) \sum_\nu F_\nu(r, t_{k+1/2})\, \Upsilon_\nu(\Omega) = \left(1 - i\frac{\Delta t}{2\hbar}\hat{H}_0(r, \Omega)\right) \sum_\nu F_\nu(r, t_k)\, \Upsilon_\nu(\Omega) \tag{2.27}$$

or, since these operators are linear,

$$\sum_\nu \left(1 + i\frac{\Delta t}{2\hbar}\hat{H}_0(r, \Omega)\right) F_\nu(r, t_{k+1/2})\, \Upsilon_\nu(\Omega) = \sum_\nu \left(1 - i\frac{\Delta t}{2\hbar}\hat{H}_0(r, \Omega)\right) F_\nu(r, t_k)\, \Upsilon_\nu(\Omega), \tag{2.28}$$

where

$$\hat{H}_0(r, \Omega) = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{\mu r}\frac{\partial}{\partial r} + \frac{\hat{L}^2}{2\mu r^2} - \kappa\frac{e^2}{r}. \tag{2.29}$$

Looking at this equation term by term, we see that since Υ_ν is an eigenfunction of $\hat{L}^2$ with eigenvalue $l_\nu(l_\nu + 1)\hbar^2$, and since Υ_ν is unaffected by the rest of the terms in the operators

$(1 \pm i\frac{\Delta t}{2\hbar}\hat{H}_0)$, we may pull Υ_ν through the operators to obtain

$$\sum_\nu \Upsilon_\nu(\Omega)\left(1 + i\frac{\Delta t}{2\hbar}\hat{H}_{0\nu}(r,\Omega)\right)F_\nu(r,t_{k+1/2}) = \sum_\nu \Upsilon_\nu(\Omega)\left(1 - i\frac{\Delta t}{2\hbar}\hat{H}_{0\nu}(r,\Omega)\right)F_\nu(r,t_k), \tag{2.30}$$

where

$$\hat{H}_{0\nu}(r,\Omega) = \hat{H}_{0\nu}(r) = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{\mu r}\frac{\partial}{\partial r} + \frac{l_\nu(l_\nu+1)\hbar^2}{2\mu r^2} - \kappa\frac{e^2}{r}. \tag{2.31}$$

Since each Υ_ν is linearly independent, we can see that this equation is really a series of independent equations, ν in quantity. Furthermore, for each of these equations Υ_ν is irrelevant and may be cancelled, so we have ν independent equations of the form

$$\left(1 + i\frac{\Delta t}{2\hbar}\hat{H}_{0\nu}(r)\right)F_\nu(r,t_{k+1/2}) = \left(1 - i\frac{\Delta t}{2\hbar}\hat{H}_{0\nu}(r)\right)F_\nu(r,t_k). \tag{2.32}$$

Of course, all of this mathematics may also be expressed in bra-ket and matrix and vector notation. If we examine the matrix elements of the pertinent operators in the Υ_ν basis, then we see

$$\begin{aligned}
\left\langle \Upsilon_\mu \middle| \left(1 \pm i\frac{\Delta t}{2\hbar}\hat{H}_0\right) \middle| \Upsilon_\nu \right\rangle &= \langle\Upsilon_\mu|\left(1 \pm i\frac{\Delta t}{2\hbar}\hat{H}_{0\nu}\right)|\Upsilon_\nu\rangle \\
&= \left(1 \pm i\frac{\Delta t}{2\hbar}\hat{H}_{0\nu}\right)\langle\Upsilon_\mu|\Upsilon_\nu\rangle \\
&= \left(1 \pm i\frac{\Delta t}{2\hbar}\hat{H}_{0\nu}\right)\delta_{\mu\nu},
\end{aligned} \tag{2.33}$$

where $\delta_{\mu\nu}$ is the Kronecker delta. Thus, we have

$$\left(1 \pm i\frac{\Delta t}{2\hbar}\hat{H}_0\right)\Psi^M(r,t) =$$

$$\begin{bmatrix}
\left(1 \pm i\frac{\Delta t}{2\hbar}\hat{H}_{01}\right) & 0 & 0 & \cdots \\
0 & \left(1 \pm i\frac{\Delta t}{2\hbar}\hat{H}_{02}\right) & 0 & \cdots \\
0 & 0 & \left(1 \pm i\frac{\Delta t}{2\hbar}\hat{H}_{03}\right) & \cdots \\
\vdots & \vdots & \vdots & \ddots
\end{bmatrix}
\begin{bmatrix} F_1(r,t) \\ F_2(r,t) \\ F_3(r,t) \\ \vdots \end{bmatrix}. \tag{2.34}$$

So, if we write Equation 2.20 using vector component notation, we have

$$\left(1 + i\frac{\Delta t}{2\hbar}\hat{H}_{0\nu}(r)\right)\Psi^M_\nu(r,t_{k+1/2}) = \left(1 - i\frac{\Delta t}{2\hbar}\hat{H}_{0\nu}(r)\right)\Psi^M_\nu(r,t_k), \tag{2.35}$$

or

$$\left(1 + i\frac{\Delta t}{2\hbar}\hat{H}_{0\nu}(r)\right)F_\nu(r,t_{k+1/2}) = \left(1 - i\frac{\Delta t}{2\hbar}\hat{H}_{0\nu}(r)\right)F_\nu(r,t_k), \tag{2.36}$$

as we found before.

That's enough for the momentum-space representation. Now we would like to discuss the coordinate-space representation, which is most appropriate for the operators $(1 \pm i\frac{\Delta t}{2\hbar}\hat{h})$. We presently make a third claim about the manner in which Ψ may be represented:

$$\Psi(r,t,\Omega) = G_\Omega(r,t). \tag{2.37}$$

Here, G_Ω is a complex function on the non-negative reals r and t. In this respect G_Ω is like F_ν. However, G_Ω is associated with a particular point $\Omega=(\theta,\phi)$ in angular coordinate space rather than with a particular momentum eigenstate Υ_ν, as F_ν is. Since θ ranges from 0 to π and ϕ ranges from 0 to 2π, Ω represents one of uncountably infinitely many points. It is possible to label each of these points with a distinct real number, so we can give a subscript α to Ω that ranges from, say, one to infinity. So letting $\Omega_\alpha=(\theta_\alpha,\phi_\alpha)$, where α is an element of the interval $(1,\infty)$, allows us to "list" these points. We can turn Ψ into a kind of column vector using this list and simplify our notation by setting $G_{\Omega_\alpha} \equiv G_\alpha$. We define $\Psi^C(r,t)$ to be the coordinate-space representation of $\Psi(r,t,\Omega)$ so that

$$\Psi^C(r,t) = \big(G_\alpha(r,t)\big)_{\alpha\in(1,\infty)} = \begin{bmatrix} G_1(r,t) \\ \vdots \\ G_2(r,t) \\ \vdots \\ G_3(r,t) \\ \vdots \end{bmatrix}. \tag{2.38}$$

Again we have the component notation $\Psi^C_\alpha(r,t)=G_\alpha$, where there are uncountably many components.

We are interested in representing the operators $(1 \pm i\frac{\Delta t}{2\hbar}\hat{h})$ in this vector space as well. Let's stay with the vector notation and find the operator's matrix elements:

$$\begin{aligned} \left\langle \Omega_\alpha \middle| \left(1 \pm i\frac{\Delta t}{2\hbar}\hat{h}\right) \middle| \Omega_\beta \right\rangle &= \langle\Omega_\alpha| \left(1 \pm i\frac{\Delta t}{2\hbar}\hat{h}_\beta\right) |\Omega_\beta\rangle \\ &= \left(1 \pm i\frac{\Delta t}{2\hbar}\hat{h}_\beta\right) \langle\Omega_\alpha|\Omega_\beta\rangle \\ &= \left(1 \pm i\frac{\Delta t}{2\hbar}\hat{h}_\beta\right) \delta_{\alpha\beta}, \end{aligned} \tag{2.39}$$

where

$$\hat{h}_\beta(r,t) = Er\cos\theta_\beta \sin\omega t. \tag{2.40}$$

Just as the operators $(1 \pm i\frac{\Delta t}{2\hbar}\hat{H}_0)$ were diagonal in their momentum-space representation, the operators $(1 \pm i\frac{\Delta t}{2\hbar}\hat{h})$ are diagonal in their coordinate-space representation:

$$\left(1 \pm i\frac{\Delta t}{2\hbar}\hat{h}\right)\Psi^C(r,t)$$

$$= \begin{bmatrix} \left(1 \pm i\frac{\Delta t}{2\hbar}\hat{h}_1\right) & \cdots & 0 & \cdots & 0 & \cdots \\ \vdots & \ddots & \vdots & \ddots & \vdots & \cdots \\ 0 & \cdots & \left(1 \pm i\frac{\Delta t}{2\hbar}\hat{h}_2\right) & \cdots & 0 & \cdots \\ \vdots & \ddots & \vdots & \ddots & \vdots & \cdots \\ 0 & \cdots & 0 & \cdots & \left(1 \pm i\frac{\Delta t}{2\hbar}\hat{h}_3\right) & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{bmatrix} \begin{bmatrix} G_1(r,t) \\ \vdots \\ G_2(r,t) \\ \vdots \\ G_3(r,t) \\ \vdots \end{bmatrix}. \qquad (2.41)$$

So, if we write Equation 2.21 in vector component notation, then it takes this form:

$$\left(1 + i\frac{\Delta t}{2\hbar}\hat{h}_\alpha(r,t_k)\right)\Psi^C_\alpha(r,t_{k+1}) = \left(1 - i\frac{\Delta t}{2\hbar}\hat{h}_\alpha(r,t_k)\right)\Psi^C_\alpha(r,t_{k+1/2}), \qquad (2.42)$$

or

$$\left(1 + i\frac{\Delta t}{2\hbar}\hat{h}_\alpha(r,t_k)\right)G_\alpha(r,t_{k+1}) = \left(1 - i\frac{\Delta t}{2\hbar}\hat{h}_\alpha(r,t_k)\right)G_\alpha(r,t_{k+1/2}). \qquad (2.43)$$

Now, Equations 2.36 and 2.43 are what we were looking for, but they of little use to us if we do not know how to move between the two representations. We need an identity transformation I that will take a wavefunction in the coordinate-space representation and return its momentum-space representation, and we need its inverse I^{-1} to take us in the opposite direction: $\Psi^M = I(\Psi^C)$ and $\Psi^C = I^{-1}(\Psi^M)$. Well, if we look at the equation

$$\Psi(r,t,\Omega) = \sum_\nu F_\nu(r,t)\,\Upsilon_\nu(\Omega) = G_\Omega(r,t), \qquad (2.44)$$

then we see that we conveniently have an orthonormal set $\{\Upsilon_\nu\}$ that relates F_ν and G_Ω. The relation between the two is thus $\langle\Upsilon_\nu|G_\Omega\rangle = F_\nu$, or, more verbosely,

$$\begin{aligned} \int \Upsilon^*_\nu(\Omega)\,G_\Omega(r,t)\,d\Omega &= \int \Upsilon^*_\nu(\Omega)\sum_{\nu'} F_{\nu'}(r,t)\,\Upsilon_{\nu'}(\Omega)\,d\Omega \\ &= \sum_{\nu'} F_{\nu'}(r,t)\int \Upsilon^*_\nu(\Omega)\,\Upsilon_{\nu'}(\Omega)\,d\Omega \\ &= \sum_{\nu'} F_{\nu'}(r,t)\,\delta_{\nu\nu'} \\ &= F_\nu(r,t). \end{aligned} \qquad (2.45)$$

All of these steps are fine, but if we translate them into matrix and vector notation, we will have some difficulties. These difficulties naturally arise when one tries to turn an integration into a matrix operation, but we might as well take a look at that process to get a feel for how our eventual numerical integration will work. We'll take our infinite "integration" matrix and turn it into a finite quadrature matrix, reducing the problem to a finite number of equations and enabling the use of a computerized numerical program.

Alright, then; let's find that matrix. We should start by defining what we mean by integration. Let

$$\int f(\Omega)\,d\Omega \equiv \lim_{\Delta\theta_j,\Delta\phi_j \to 0} \sum_{j=1}^{M} f(\Omega_j)\,\sin\theta_j\,\Delta\theta_j\,\Delta\phi_j, \qquad (2.46)$$

where the limit implies that the number of points M approaches infinity and the mesh[6] of the partition approaches zero. Then the first integral in Equations 2.45 becomes

$$\begin{aligned}
\int \Upsilon_\nu^*(\Omega)\, G_\Omega(r,t)\, d\Omega &= \lim_{\Delta\theta_j, \Delta\phi_j \to 0} \sum_{j=1}^{N} \Upsilon_\nu^*(\Omega_j)\, G_j(r,t)\, \sin\theta_j\, \Delta\theta_j\, \Delta\phi_j \\
&= \lim_{\Delta\theta_j, \Delta\phi_j \to 0} \sum_{j=1}^{N} \Upsilon_\nu^*(\Omega_j) \sum_{\nu'} F_{\nu'}(r,t)\, \Upsilon_{\nu'}(\Omega)\, \sin\theta_j\, \Delta\theta_j\, \Delta\phi_j \\
&= \sum_{\nu'} F_{\nu'}(r,t) \lim_{\Delta\theta_j, \Delta\phi_j \to 0} \sum_{j=1}^{N} \Upsilon_\nu^*(\Omega_j)\, \Upsilon_{\nu'}(\Omega)\, \sin\theta_j\, \Delta\theta_j\, \Delta\phi_j \\
&= \sum_{\nu'} F_{\nu'}(r,t)\, \delta_{\nu\nu'} \\
&= F_\nu(r,t). \qquad (2.47)
\end{aligned}$$

So we have, in matrix notation,

$$\Psi^M(r,t) = \begin{bmatrix} F_1(r,t) \\ F_2(r,t) \\ F_3(r,t) \\ \vdots \end{bmatrix}$$

$$= \lim_{\Delta\theta_j, \Delta\phi_j \to 0} \begin{bmatrix} \Upsilon_1^*(\Omega_{j1})\, sin\theta_{j1}\, \Delta\theta_{j1}\, \Delta\phi_{j1} & \Upsilon_1^*(\Omega_{j2})\, sin\theta_{j2}\, \Delta\theta_{j2}\, \Delta\phi_{j2} & \cdots \\ Y_2^*(\Omega_{j1})\, sin\theta_{j1}\, \Delta\theta_{j1}\, \Delta\phi_{j1} & \Upsilon_2^*(\Omega_{j2})\, sin\theta_{j2}\, \Delta\theta_{j2}\, \Delta\phi_{j2} & \cdots \\ Y_3^*(\Omega_{j1})\, sin\theta_{j1}\, \Delta\theta_{j1}\, \Delta\phi_{j1} & \Upsilon_3^*(\Omega_{j2})\, sin\theta_{j2}\, \Delta\theta_{j2}\, \Delta\phi_{j2} & \cdots \\ \vdots & \vdots & \ddots \end{bmatrix} \begin{bmatrix} G_{j1}(r,t) \\ G_{j2}(r,t) \\ G_{j3}(r,t) \\ \vdots \end{bmatrix}, \qquad (2.48)$$

where the j-values ($j1, j2, j3$, etc.) are determined by the particular partition. We can define this integral a bit more loosely by imagining that we can actually take the limit and produce a simple matrix and vector equation. In the limit, each $\Delta\theta_j\, \Delta\phi_j$ would become infinitesimal, and they could all be factored out of the matrix. Also, the vector with the G_j components would become our familiar Ψ^C:

$$\Psi^M(r,t) = \begin{bmatrix} F_1(r,t) \\ F_2(r,t) \\ F_3(r,t) \\ \vdots \end{bmatrix}$$

$$= \begin{bmatrix} \Upsilon_1^*(\Omega_1)\, sin\theta_1 & \cdots & \Upsilon_1^*(\Omega_2)\, sin\theta_2 & \cdots & \Upsilon_1^*(\Omega_3)\, sin\theta_3 & \cdots \\ \Upsilon_2^*(\Omega_1)\, sin\theta_1 & \cdots & \Upsilon_2^*(\Omega_2)\, sin\theta_2 & \cdots & \Upsilon_2^*(\Omega_3)\, sin\theta_3 & \cdots \\ \Upsilon_3^*(\Omega_1)\, sin\theta_1 & \cdots & \Upsilon_3^*(\Omega_2)\, sin\theta_2 & \cdots & \Upsilon_3^*(\Omega_3)\, sin\theta_3 & \cdots \\ \vdots & \vdots & \vdots & \vdots & \vdots & \ddots \end{bmatrix} d\theta\, d\phi \begin{bmatrix} G_1(r,t) \\ \vdots \\ G_2(r,t) \\ \vdots \\ G_3(r,t) \\ \vdots \end{bmatrix}$$

---

[6] In this two-dimensional case, the mesh of the partition is the largest area $\Delta\theta_j\, \Delta\phi_j$ determined by the partition of the angular coordinate space.

$$= I\,\Psi^C(r,t). \tag{2.49}$$

So we have now found the matrix form of our transformation I. Of course, this loose matrix version of the integral is not a practical transformation if we are going to be using actual numbers. We don't want to have to deal with infinitessimals or with uncountably infinitely many elements, or countably infinitely many for that matter. What we need to do now is reduce each vector to a finite number of components and find an approximate version of this integration transformation that is invertible. What we need to do is to discretize the angular coordinates and come up with a means for numerical integration.

2.2.3 Discrete Angular Coordinates and Quadrature

Let's recapitulate what has happened so far in our quest to solve Schrödinger's equation. We have discretized the time variable to escape the intractability of the analytical approach. We have found a nice replacement propagator that happens to separate the operator with $\hat{H}_0$, which affects angular coordinates, and the operator with $\hat{h}$, which is merely coordinate-dependent. We thereby came up with two equations that are most conveniently represented in different bases. And now we have determined that to move back and forth between the two representations, we should discretize the angular coordinates and come up with a means for numerical integration.

We shall overcome this current predicament by using a special technique of numerical integration called Gaussian quadrature. In the context of geometry, quadrature refers to the construction of a square with the same area as a given shape or surface. In the context of integration of a real function of one variable, quadrature refers to the approximation of a definite integral of a function essentially by summing the signed areas of multiple rectangles that approximate the signed area between the given function and the axis of the independent variable. Quadrature is therefore synonymous with numerical integration. Quadrature also refers to multidimensional numerical integration, which is sometimes called cubature. In our case we will use a complex two-dimensional N-point Gaussian quadrature rule. We will use this quadrature rule to integrate the function $\Upsilon^*(\theta,\phi)\,G(r,t)$ over the two variables θ and ϕ using discrete points.

Using Gaussian quadrature, we may specify N, the number of points we wish to use, and the rest is mathematically optimized: the locations of the points Ω_j are determined and weights ω_j are determined such that

$$\sum_j \omega_j\,\Upsilon^*_\nu(\Omega_j)\,\Upsilon_{\nu'}(\Omega_j) \;=\; \int \Upsilon^*_\nu(\Omega)\,\Upsilon_{\nu'}(\Omega)\,d\Omega \;=\; \delta_{\nu\nu'}, \tag{2.50}$$

which implies that

$$\sum_m \sum_{m'} O^*_{pm}\,O_{p'm'} \left(\sum_j \omega_j\, Y^*_{lm}(\Omega_j)\, Y_{l'm'}(\Omega_j) \right) \;=\; \delta_{\nu\nu'} \;=\; \delta_{ll'pp'} \;=\; \delta_{ll'}\delta_{pp'}. \tag{2.51}$$

So, we therefore have

$$\sum_j \omega_j\,\Upsilon^*_\nu(\Omega_j)\,G_j(r,t) \;=\; \int \Upsilon^*_\nu(\Omega)\,G_\Omega(r,t)\,d\Omega \;=\; F_\nu(r,t). \tag{2.52}$$

Then, if we denote this discretization with a tilde over the wavefunciton like so, $\widetilde{\Psi}$, then we have

$$
\begin{aligned}
\Psi^M(r,t) &= \begin{bmatrix} F_1(r,t) \\ F_2(r,t) \\ F_3(r,t) \\ \vdots \end{bmatrix} \\
&= \begin{bmatrix} \omega_1\,\Upsilon_1^*(\Omega_1) & \omega_2\,\Upsilon_1^*(\Omega_2) & \cdots & \omega_N\,\Upsilon_1^*(\Omega_N) \\ \omega_1\,\Upsilon_2^*(\Omega_1) & \omega_2\,\Upsilon_2^*(\Omega_2) & \cdots & \omega_N\,\Upsilon_2^*(\Omega_N) \\ \omega_1\,\Upsilon_3^*(\Omega_1) & \omega_2\,\Upsilon_3^*(\Omega_2) & \cdots & \omega_N\,\Upsilon_3^*(\Omega_N) \\ \vdots & \vdots & \cdots & \vdots \end{bmatrix} \begin{bmatrix} G_1(r,t) \\ G_2(r,t) \\ \vdots \\ G_N(r,t) \end{bmatrix} \\
&= \widetilde{I}\,\widetilde{\Psi}^C(r,t). \qquad (2.53)
\end{aligned}
$$

Note that Ψ^M is not affected by this change. We have here a transformation matrix $\widetilde{I}$ that has N columns of countably infinite length. What we want, however, is an invertible matrix, so we have to cut the length of these columns to make $\widetilde{I}$ a square matrix. Somehow, then, we have to determine which spherical harmonics shall take precedence in our problem. We shall take the approach of using the lowest possible values first, so the order of preference will go like this: $\nu_1 = (0,0)$, $\nu_2 = (1,0)$, $\nu_3 = (1,-1)$, $\nu_4 = (1,1)$, $\nu_5 = (2,0)$, $\nu_6 = (2,-1)$, $\nu_7 = (2,1)$, $\nu_8 = (2,-2)$, $\nu_9 = (2,2)$, and so on until we have N spherical harmonics. Now, if we use another tilde to denote the finite version of Ψ^M and if we call the final truncated transformation Q for "quadrature" or "questionably sufficiently many momentum states," then we have

$$
\begin{aligned}
\widetilde{\Psi}^M(r,t) &= \begin{bmatrix} F_1(r,t) \\ F_2(r,t) \\ \vdots \\ F_N(r,t) \end{bmatrix} \\
&= \begin{bmatrix} \omega_1\,\Upsilon_1^*(\Omega_1) & \omega_2\,\Upsilon_1^*(\Omega_2) & \cdots & \omega_N\,\Upsilon_1^*(\Omega_N) \\ \omega_1\,\Upsilon_2^*(\Omega_1) & \omega_2\,\Upsilon_2^*(\Omega_2) & \cdots & \omega_N\,\Upsilon_2^*(\Omega_N) \\ \vdots & \vdots & \ddots & \vdots \\ \omega_1\,\Upsilon_N^*(\Omega_1) & \omega_2\,\Upsilon_N^*(\Omega_2) & \cdots & \omega_N\,\Upsilon_N^*(\Omega_N) \end{bmatrix} \begin{bmatrix} G_1(r,t) \\ G_2(r,t) \\ \vdots \\ G_N(r,t) \end{bmatrix} \\
&= Q\,\widetilde{\Psi}^C(r,t), \qquad (2.54)
\end{aligned}
$$

and we have finally found the desired transformation, assuming that Q is actually invertible. Now we can move back and forth between the two representations and attempt to solve the two vector equations (or $2N$ scalar equations) that will propagate our approximate solution wavefunction through time.

2.2.4 Discrete Radial Coordinates, Splines, and More Quadrature

We want to solve Equations 2.36 and 2.43, shown again here:

$$\left(1 + i\frac{\Delta t}{2\hbar}\hat{H}_{0\nu}(r)\right) F_\nu(r, t_{k+1/2}) \quad = \quad \left(1 - i\frac{\Delta t}{2\hbar}\hat{H}_{0\nu}(r)\right) F_\nu(r, t_k) \qquad (2.55)$$

$$\left(1+i\frac{\Delta t}{2\hbar}\hat{h}_j(r,t_k)\right)G_j(r,t_{k+1}) \quad = \quad \left(1-i\frac{\Delta t}{2\hbar}\hat{h}_j(r,t_k)\right)G_j(r,t_{k+1/2}) \tag{2.56}$$

Remember that ν takes N different values and j takes N different values, yielding a total of $2N$ equations, and remember that

$$\hat{H}_{0\nu}(r) = -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{\mu r}\frac{\partial}{\partial r} + \frac{l_\nu(l_\nu+1)\hbar^2}{2\mu r^2} - \kappa\frac{e^2}{r} \tag{2.57}$$

and

$$\hat{h}_j(r,t) = Er\cos\theta_j\sin\omega t. \tag{2.58}$$

Thus there are N differential equations and N linear equations. These are quite complicated equations, especially given that $F_\nu(r,t_k)$ and $G_j(r,t_k)$ are complex functions.

Our first consideration in moving closer to a solution is the boundary conditions. We will start by taking a step in analogy with the regular hydrogen problem. In that simpler problem we had the relationship $U=rR$, where the radial wavefunction could be multiplied by r to yield the the function U, whose magnitude squared is the radial probability density funcion. The function U had the Dirichlet boundary condition of equalling zero at the origin and at infinity. This is a nice condition to have in a differential equation, so we will mirror this procedure and multiply our radial functions F_ν and G_j by r to yield the functions V_ν and W_j:

$$V_\nu(r,t) = r\,F_\nu(r,t) \tag{2.59}$$

and

$$W_j(r,t) = r\,G_j(r,t), \tag{2.60}$$

where V_ν and W_j are complex functions. Thinking of vector notation again, let's define

$$\widetilde{\mathcal{U}}^M(r,t) = r\,\widetilde{\Psi}^M(r,t) \tag{2.61}$$

and

$$\widetilde{\mathcal{U}}^C(r,t) = r\,\widetilde{\Psi}^C(r,t), \tag{2.62}$$

where $V_\nu = \widetilde{\mathcal{U}}^M_\nu(r,t)$ and $W_j = \widetilde{\mathcal{U}}^C_j(r,t)$. As it happens, multiplying by r does not change the transformation Q between the two representations, so $\widetilde{\mathcal{U}}^M(r,t) = Q\,\widetilde{\mathcal{U}}^C(r,t)$. As was the case in the original hydrogen problem, the hamiltonian $\hat{H}_{0\nu}$ will become more simple after this transformation; $\hat{h}_j$, however, will remain the same. Equations 2.55 and 2.56 thus become

$$\begin{aligned}&\left[1+i\frac{\Delta t}{2\hbar}\left(-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2}+\frac{l_\nu(l_\nu+1)\hbar^2}{2\mu r^2}-\kappa\frac{e^2}{r}\right)\right]V_\nu(r,t_{k+1/2})\\ &= \left[1-i\frac{\Delta t}{2\hbar}\left(-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2}+\frac{l_\nu(l_\nu+1)\hbar^2}{2\mu r^2}-\kappa\frac{e^2}{r}\right)\right]V_\nu(r,t_k)\end{aligned} \tag{2.63}$$

and

$$\left[1+i\frac{\Delta t}{2\hbar}\left(Er\cos\theta_j\sin\omega t_k\right)\right]W_j(r,t_{k+1}) \;=\; \left[1-i\frac{\Delta t}{2\hbar}\left(Er\cos\theta_j\sin\omega t_k\right)\right]W_j(r,t_{k+1/2}). \tag{2.64}$$

Next we shall use a numerical technique involving splines to solve the differential equations. In mathematics, splines are piecewise-defined polynomials that are used to fit a curve to a discrete set of data points (a.k.a. nodes or knots). The name spline may refer to the individual piecewise-defined polynomials or the resulting fitted curve. If we sample our initial wavefunction at a finite number N_s of radial positions[7], then we will be able to represent it approximately with these interpolated polynomials, which are easily differentiated. Specifically, we shall approximate the two complex functions V_ν and W_j using overlapping segments of real fifth degree polynomials, or splines, multiplied by complex coefficients. We will also approximate the first and second derivatives of each function using fifth degree splines. In this way we can force the whole wavefunction and its first and second derivatives to be continuous everywhere with respect to r by requiring that the splines be continuous at the end points of the segments. The chosen radial points furthest from the origin should be located far away enough such that the functions at these locations are essentially zero for all time; thus we will meet the outer Dirichlet boundary condition for the functions and ensure that we don't have reflections of our solution from the boundary.

Let's look in detail at each of the splines we are using for these functions. First, assume we have selected the N_s radial points starting with $r_1 = 0$ and ending with r_{N_s}. We are free to pick these points as we desire. These points are not necessarily evenly spaced; in fact, it's better if they are less dense further from the origin since the functions will approach zero, become flat, and be easily described by fewer points. Anyway, let $r_{\iota-1}, r_\iota$, and $r_{\iota+1}$ be three consecutive points; each interval $(r_{\iota-1}, r_{\iota+1})$ determined by such a set will have three pairs of piecewise-defined polynomials, where one pair determines the value at r_ι, another pair determines the first derivative at r_ι, and the last pair determines the second derivative at r_ι.

The first pair of polynomials is shown in Figure 1. On the left side, from $r_{\iota-1}$ to r_ι, is $S_{\iota 00}$, and on the right side, from r_ι to $r_{\iota+1}$, is $S_{\iota 01}$. Let

$$S_{\iota 00}(r) = s_{\iota 000} + s_{\iota 001} r + s_{\iota 002} r^2 + s_{\iota 003} r^3 + s_{\iota 004} r^4 + s_{\iota 005} r^5 \tag{2.65}$$

such that

$$\begin{aligned} S_{\iota 00}(r_{\iota-1}) &= S_{\iota 00}{}'(r_{\iota-1}) = S_{\iota 00}{}''(r_{\iota-1}) = 0 \\ S_{\iota 00}(r_\iota) &= 1,\ S_{\iota 00}{}'(r_\iota) = S_{\iota 00}{}''(r_\iota) = 0, \end{aligned} \tag{2.66}$$

and let

$$S_{\iota 01}(r) = s_{\iota 010} + s_{\iota 011} r + s_{\iota 012} r^2 + s_{\iota 013} r^3 + s_{\iota 014} r^4 + s_{\iota 015} r^5 \tag{2.67}$$

such that

$$\begin{aligned} S_{\iota 01}(r_\iota) &= 1,\ S_{\iota 01}{}'(r_\iota) = S_{\iota 01}{}''(r_\iota) = 0 \\ S_{\iota 01}(r_{\iota+1}) &= S_{\iota 01}{}'(r_{\iota+1}) = S_{\iota 01}{}''(r_{\iota+1}) = 0. \end{aligned} \tag{2.68}$$

If we multiply these polynomials by some constant, then we will ensure that the function using this spline will equal that constant at r_ι.

The second pair of polynomials is shown in Figure 2. On the left side, from $r_{\iota-1}$ to r_ι, is $S_{\iota 10}$, and on the right side, from r_ι to $r_{\iota+1}$, is $S_{\iota 11}$. Let

$$S_{\iota 10}(r) = s_{\iota 100} + s_{\iota 101} r + s_{\iota 102} r^2 + s_{\iota 103} r^3 + s_{\iota 104} r^4 + s_{\iota 105} r^5 \tag{2.69}$$

---

[7] The s in N_s stands for "spline nodes."

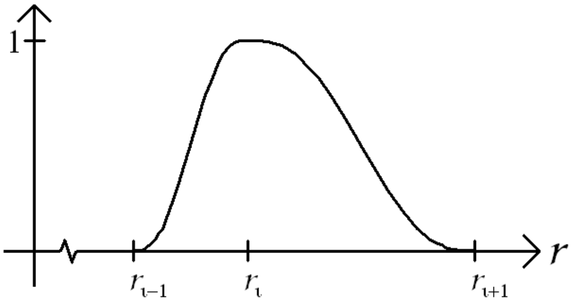

Figure 1: Spline 1: $S_{\iota 00}(r)$ for $r \in [r_{\iota-1}, r_\iota]$ and $S_{\iota 01}(r)$ for $r \in [r_\iota, r_{\iota+1}]$. See Appendix B for the explicit equations.

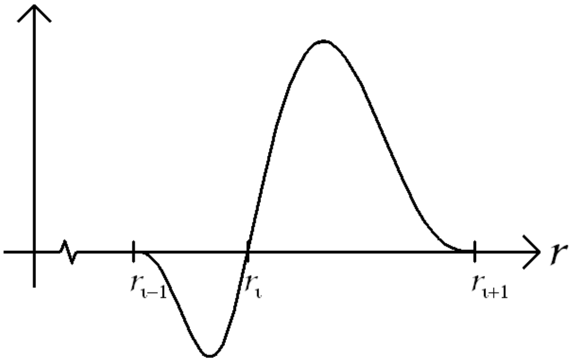

Figure 2: Spline 2: $S_{\iota 10}(r)$ for $r \in [x_{\iota-1}, r_\iota]$ and $S_{\iota 11}(r)$ for $r \in [r_\iota, r_{\iota+1}]$. See Appendix B for the explicit equations. Note that the vertical axis is not at the same scale as the vertical axis in Figure 1: Spline 2 is actually shorter than Spline 1.

such that

$$\begin{aligned} S_{\iota 10}(r_{\iota-1}) &= S_{\iota 10}{}'(r_{\iota-1}) = S_{\iota 10}{}''(r_{\iota-1}) = 0 \\ S_{\iota 10}(r_\iota) &= 0,\ S_{\iota 10}{}'(r_\iota) = 1,\ S_{\iota 10}{}''(r_\iota) = 0, \end{aligned} \tag{2.70}$$

and let

$$S_{\iota 11}(r) = s_{\iota 110} + s_{\iota 111}r + s_{\iota 112}r^2 + s_{\iota 113}r^3 + s_{\iota 114}r^4 + s_{\iota 115}r^5 \tag{2.71}$$

such that

$$\begin{aligned} S_{\iota 11}(r_\iota) &= 0,\ S_{\iota 11}{}'(r_\iota) = 1,\ S_{\iota 11}{}''(r_\iota) = 0 \\ S_{\iota 11}(r_{\iota+1}) &= S_{\iota 11}{}'(r_{\iota+1}) = S_{\iota 11}{}''(r_{\iota+1}) = 0. \end{aligned} \tag{2.72}$$

If we multiply these polynomials by some constant, then we will ensure that the function using this spline will have a first derivative equal to that constant at r_ι.

The third pair of polynomials is shown in Figure 3. On the left side, from $r_{\iota-1}$ to r_ι, is $S_{\iota 20}$, and on the right side, from r_ι to $r_{\iota+1}$, is $S_{\iota 21}$. Let

$$S_{\iota 20}(r) = s_{\iota 200} + s_{\iota 201}r + s_{\iota 202}r^2 + s_{\iota 203}r^3 + s_{\iota 204}r^4 + s_{\iota 205}r^5 \tag{2.73}$$

such that

$$S_{\iota 20}(r_{\iota-1}) = S_{\iota 20}{}'(r_{\iota-1}) = S_{\iota 20}{}''(r_{\iota-1}) = 0$$

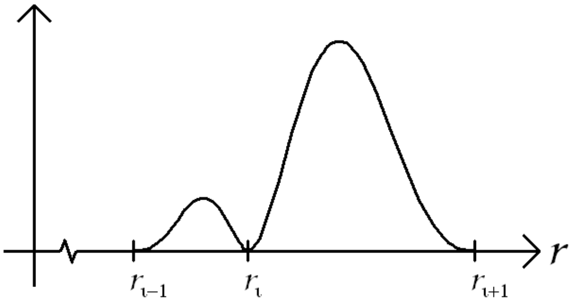

Figure 3: Spline 3: $S_{\iota 20}(r)$ for $r \in [r_{\iota-1}, r_\iota]$ and $S_{\iota 21}(r)$ for $r \in [r_\iota, r_{\iota+1}]$. See Appendix B for the explicit equations. Note that the vertical axis is not at the same scale as the vertical axis in Figure 1: Spline 3 is actually much shorter than Spline 1.

$$S_{\iota 20}(r_\iota) \;=\; {S_{\iota 20}}'(r_\iota) \;=\; 0,\; {S_{\iota 20}}''(r_\iota) \;=\; 1, \tag{2.74}$$

and let

$$S_{\iota 21}(r) = s_{\iota 210} + s_{\iota 211}r + s_{\iota 212}r^2 + s_{\iota 213}r^3 + s_{\iota 214}r^4 + s_{\iota 215}r^5 \tag{2.75}$$

such that

$$\begin{aligned} S_{\iota 21}(r_\iota) \;&=\; {S_{\iota 21}}'(r_\iota) \;=\; 0,\; {S_{\iota 21}}''(r_\iota) \;=\; 1 \\ S_{\iota 21}(r_{\iota+1}) \;&=\; {S_{\iota 21}}'(r_{\iota+1}) \;=\; {S_{\iota 21}}''(r_{\iota+1}) \;=\; 0. \end{aligned} \tag{2.76}$$

If we multiply these polynomials by some constant, then we will ensure that the function using this spline will have a second derivative equal to that constant at r_ι.

We've described one three-point interval starting at $r_{\iota-1}$ and ending at $r_{\iota+1}$, where a spline consisting of six fifth-degree polynomials characterizes the middle point r_ι. To characterize the points $r_{\iota-1}$ and $r_{\iota+1}$ we must allow additional splines to overlap: one spline must extend from $r_{\iota-2}$ to r_ι and another must extend from r_ι to $r_{\iota+2}$. In this way, all points may be characterized with overlapping splines. Only the endpoints r_1 and r_{N_s} must be treated differently since no intervals are defined before r_1 and after r_{N_s}. They will require three polynomials each instead of six; however, in Equation 2.77 below, we will define all six polynomials and simply ignore the three outside the region of interest. All of this spline business is summarized in Figure 4.

Now, we can finally mathematically represent our functions with splines:

$$V_\nu(r,t) = \sum_{\iota=1}^{N_s} \sum_{\zeta=0}^{2} \sum_{\xi=0}^{1} v_{\iota\zeta}^{\nu}(t)\, S_{\iota\zeta\xi}(r), \tag{2.77}$$

where the coefficient function $v_{\iota\zeta}^{\nu}(t)$ is complex. The same goes for $W_j(r,t)$, except its coefficient function is $w_{\iota\zeta}^{j}(t)$. Since we are defining these functions only from $r_1 = 0$ to r_{N_s}, we may ignore those functions defined outside of this interval: $S_{0\zeta 0}$ and $S_{N_s\zeta 1}$. These functions were included merely to keep the summation simple. Given Equation 2.77 and the preceding explanations, you should agree with the following relations:

$$V_\nu(r_\iota,t) \;=\; v_{\iota 0}^{\nu}(t) S_{\iota 00}(r_\iota) \;=\; v_{\iota 0}^{\nu}(t) S_{\iota 01}(r_\iota) \;=\; v_{\iota 0}^{\nu}(t) \tag{2.78}$$

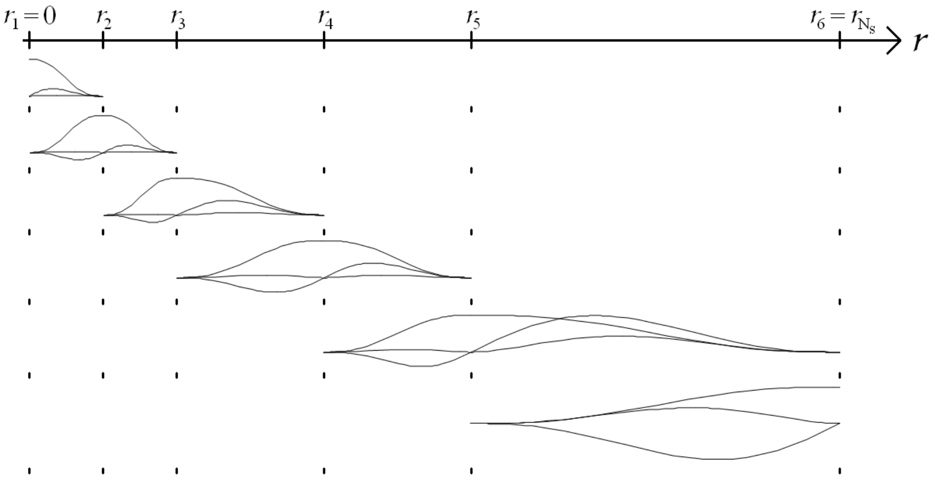

Figure 4: This diagram illustrates how the splines cover overlapping intervals, given $N_s = 6$. It also illustrates how small the splines characterizing the second derivative are compared with the other two splines: they look essentially flat until the node points spread out. These splines are multiplied by complex numbers and added together to construct the wavefunction at some point in time.

$$V_\nu{}'(r_\iota, t) \; = \; v^\nu_{\iota 1}(t) S_{\iota 10}(r_\iota) \; = \; v^\nu_{\iota 1}(t) S_{\iota 11}(r_\iota) \; = \; v^\nu_{\iota 1}(t) \tag{2.79}$$

$$V_\nu{}''(r_\iota, t) \; = \; v^\nu_{\iota 2}(t) S_{\iota 20}(r_\iota) \; = \; v^\nu_{\iota 2}(t) S_{\iota 21}(r_\iota) \; = \; v^\nu_{\iota 2}(t) \tag{2.80}$$

Due to the boundary conditions, both $v^\nu_{00}(t)$ and $v^\nu_{N_s 0}(t)$ must be zero. We will find later on that it will also be very convenient for us to set another coefficient to zero: we pick $v^\nu_{N_s 1}(t)$ since it should be extremely close to zero anyway. We'll just say it's zero now and explain why that's helpful later. If we look at the first derivative of V_ν at points other than the r_ι's, we simply have

$$V_\nu{}'(r, t) \; = \; \sum_{\iota=1}^{N_s} \sum_{\zeta=0}^{2} \sum_{\xi=0}^{1} v^\nu_{\iota\zeta}(t) \, S_{\iota\zeta\xi}{}'(r). \tag{2.81}$$

Similar relations apply for $W_j{}'$ and the second derivatives. Since the splines $S_{\iota\zeta\xi}$ are all determined once the radial points are picked, their derivatives $S_{\iota\zeta\xi}{}'$ and $S_{\iota\zeta\xi}{}''$ are also determined and known. It is the coefficients $v^\nu_{\iota\zeta}(t)$ and $w^j_{\iota\zeta}(t)$ for $t > 0$ that will be unknown in our equations that propagate the wavefunction.

Although our notation so far has been quite explicit and clear, three indices and summation signs will become bothersome if we carry on in this manner. To whittle our way down to one index, we can first piece together each associated pair of splines that have the same coefficient; that gets rid of the ξ index and one summation. Then we can "telescope out" (i.e. expand) the remaining double summation and name each term with only one index: s. The order will be determined by first running through the ζ index and then the ι index. We will also leave out the splines that we already know are multiplied by zero. Thus, we have defined v^ν_s, w^j_s, and S_s, where $S_1 = S_{110} + S_{111}$, $S_2 = S_{120} + S_{121}$, $S_3 = S_{200} + S_{201}$, $S_4 = S_{210} + S_{211}$, $S_5 = S_{220} + S_{221}$, and so on. The index s, as it stands now, ranges from 1 to $3N_s - 3$, so we have

$$V_\nu(r,t) = \sum_{s=1}^{3N_s-3} v_s^\nu(t)\, S_s(r), \tag{2.82}$$

and similarly for W_j. Since the splines are a linearly independent set and we are using them as an approximate basis, each V_ν and W_j may be represented as a row vector and the $\widetilde{U}$'s may thereby be represented as matrices. Rather than coming up with a new name, we can just see w_s^j and v_s^ν as the elements of the matrices w and v, where the superscripts indicate the row number and the subscripts indicate the column number. We may further consider v_s to denote the columns of the matrix v and v^ν to denote the rows. With this notation, we still have the same transformation matrix as before, $v(t) = Q\, w(t)$, so long as we insure that N, the number of momentum states and angular points, equals $3N_s - 3$, the number of splines.

With our new representations of V_ν and W_j, we may now look again at Equations 2.63 and 2.64. If we replace V_ν and W_j with their series forms, as illustrated in Equation 2.82, then we can rearrange the equations like so:

$$\begin{aligned}&\sum_{s=1}^{3N_s-3}\left[\left\{1 + i\Delta t\left(\frac{l_\nu(l_\nu+1)\hbar}{4\mu r^2} - \kappa\frac{e^2}{2\hbar r}\right)\right\} S_s(r) - \left\{i\Delta t\frac{\hbar}{4\mu}\right\} S_s{}''(r)\right] v_s^\nu(t_{k+1/2})\\ &= \sum_{s=1}^{3N_s-3}\left[\left\{1 - i\Delta t\left(\frac{l_\nu(l_\nu+1)\hbar}{4\mu r^2} - \kappa\frac{e^2}{2\hbar r}\right)\right\} S_s(r) - \left\{i\Delta t\frac{\hbar}{4\mu}\right\} S_s{}''(r)\right] v_s^\nu(t_k)\end{aligned} \tag{2.83}$$

and

$$\begin{aligned}&\sum_{s=1}^{3N_s-3}\left[\left\{1 + i\frac{\Delta t}{2\hbar}\left(Er\cos\theta_j\sin\omega t_k\right)\right\} S_s(r)\right] w_s^j(t_{k+1})\\ &= \sum_{s=1}^{3N_s-3}\left[\left\{1 - i\frac{\Delta t}{2\hbar}\left(Er\cos\theta_j\sin\omega t_k\right)\right\} S_s(r)\right] w_s^j(t_{k+1/2}).\end{aligned} \tag{2.84}$$

All of this will look much simpler if we coalesce the terms in the square brackets into individual symbols. Letting[8]

$$\mathcal{P}_s^\nu(r) = \left\{1 + i\Delta t\left(\frac{l_\nu(l_\nu+1)\hbar}{4\mu r^2} - \kappa\frac{e^2}{2\hbar r}\right)\right\} S_s(r) - \left\{i\Delta t\frac{\hbar}{4\mu}\right\} S_s{}''(r), \tag{2.85}$$

$$\mathcal{M}_s^\nu(r) = \left\{1 - i\Delta t\left(\frac{l_\nu(l_\nu+1)\hbar}{4\mu r^2} - \kappa\frac{e^2}{2\hbar r}\right)\right\} S_s(r) - \left\{i\Delta t\frac{\hbar}{4\mu}\right\} S_s{}''(r), \tag{2.86}$$

$$\mathcal{P}_s^j(r,t_k) = \left\{1 + i\frac{\Delta t}{2\hbar}\left(Er\cos\theta_j\sin\omega t_k\right)\right\} S_s(r), \tag{2.87}$$

and

$$\mathcal{M}_s^j(r,t_k) = \left\{1 - i\frac{\Delta t}{2\hbar}\left(Er\cos\theta_j\sin\omega t_k\right)\right\} S_s(r), \tag{2.88}$$

---

[8] $\mathcal{P}$ for plus and $\mathcal{M}$ for minus.

we now have

$$\sum_{s=1}^{3N_s-3} \mathcal{P}_s^\nu(r)\, v_s^\nu(t_{k+1/2}) = \sum_{s=1}^{3N_s-3} \mathcal{M}_s^\nu(r)\, v_s^\nu(t_k) \tag{2.89}$$

and

$$\sum_{s=1}^{3N_s-3} \mathcal{P}_s^j(r)\, w_s^j(t_{k+1}) = \sum_{s=1}^{3N_s-3} \mathcal{M}_s^j(r)\, w_s^j(t_{k+1/2}). \tag{2.90}$$

Since we are using these equations to propagate the coefficients into the future, we can assume we know the coefficients on the right-hand sides, $v_s^\nu(t_k)$ and $w_s^j(t_{k+1/2})$. We might as well condense the right hand sides as well: let

$$\mathcal{N}^\nu(r, t_k) = \sum_{s=1}^{3N_s-3} \mathcal{M}_s^\nu(r)\, v_s^\nu(t_k) \tag{2.91}$$

and

$$\mathcal{N}^j(r, t_{k+1/2}) = \sum_{s=1}^{3N_s-3} \mathcal{M}_s^j(r, t_k)\, w_s^j(t_{k+1/2}). \tag{2.92}$$

That leaves us with

$$\sum_{s=1}^{3N_s-3} \mathcal{P}_s^\nu(r)\, v_s^\nu(t_{k+1/2}) = \mathcal{N}^\nu(r, t_k) \tag{2.93}$$

and

$$\sum_{s=1}^{3N_s-3} \mathcal{P}_s^j(r, t_k)\, w_s^j(t_{k+1}) = \mathcal{N}^j(r, t_{k+1/2}). \tag{2.94}$$

Now, if we consider ν and j to be constant, for each of these two equations we have $3N_s-3$ unknown coefficients. The coefficients are complex and the equations are linear, so we need to have the same number of equations as there are unknowns to solve for the unknowns. We need to pick $3N_s-3$ radial points and evaluate these equations at those points. If we pick three new points within each $(r_\iota, r_{\iota+1})$ interval[9], then we'll have $3(N_s-1) = 3N_s–3$ equations, which is exactly what we need. (This is why we chose $v_{N_s1}^\nu(t)$ to be zero – so we would have $3N_s-3$ unknown coefficients instead of $3N_s-2$.) Let's call the number of points we pick N_r, so $N_r = 3N_s-3$. We won't just pick any random three points in each interval, though. We'll use a Gaussian quadrature rule again, this time chosen so that we may perform an integral that will later be of interest (in Equations 2.99):

$$\sum_{i=1}^{N_r} \omega_i\, R_{nl}(r_i)\, \frac{1}{r_i}\, S_s(r_i) = \int_0^{r_{N_s}} R_{nl}(r)\, \frac{1}{r}\, S_s(r) = \left\langle R_{nl}(r) \middle| \frac{1}{r} S_s(r) \right\rangle, \tag{2.95}$$

for each s. Anyway, once these collocation points are chosen we have everything we need to solve our problem.

It would be prudent to write this all out in vector notation before moving on. Let's consider only the momentum-representation for the time being and rewrite equation 2.93.

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[9] These newly chosen radial points will be called collocation points, as distinguished from the nodes that were picked for the splines. They are collocated in triples within each interval between the nodes.

We've already described v^ν as a row vector, but since we all seem to love dealing with column vectors and multiplying them by matrices from the right, we'll write v^ν as a column vector here rather than a row vector. We have

$$\begin{bmatrix} \mathcal{P}_1^\nu(r) & \mathcal{P}_2^\nu(r) & \cdots & \mathcal{P}_{N_r}^\nu(r) \end{bmatrix} \begin{bmatrix} v_1^\nu(t_{k+1/2}) \\ v_2^\nu(t_{k+1/2}) \\ \vdots \\ v_{N_r}^\nu(t_{k+1/2}) \end{bmatrix} = \mathcal{N}^\nu(r, t_k). \tag{2.96}$$

Then, after picking the collocation points, we have

$$\begin{bmatrix} \mathcal{P}_1^\nu(r_1) & \mathcal{P}_2^\nu(r_1) & \cdots & \mathcal{P}_{N_r}^\nu(r_1) \\ \mathcal{P}_1^\nu(r_2) & \mathcal{P}_2^\nu(r_2) & \cdots & \mathcal{P}_{N_r}^\nu(r_2) \\ \vdots & \vdots & \ddots & \vdots \\ \mathcal{P}_1^\nu(r_{N_r}) & \mathcal{P}_2^\nu(r_{N_r}) & \cdots & \mathcal{P}_{N_r}^\nu(r_{N_r}) \end{bmatrix} \begin{bmatrix} v_1^\nu(t_{k+1/2}) \\ v_2^\nu(t_{k+1/2}) \\ \vdots \\ v_{N_r}^\nu(t_{k+1/2}) \end{bmatrix} = \begin{bmatrix} \mathcal{N}^\nu(r_1, t_k) \\ \mathcal{N}^\nu(r_2, t_k) \\ \vdots \\ \mathcal{N}^\nu(r_{N_r}, t_k) \end{bmatrix}. \tag{2.97}$$

Let's call the matrix on the left $\mathcal{P}^\nu$. So long as $\mathcal{P}^\nu$ is invertible, we may thus use Gauss-Jordan elimination on the augmented matrix to solve the equation:

$$\begin{aligned} &\begin{bmatrix} \mathcal{P}_1^\nu(r_1) & \mathcal{P}_2^\nu(r_1) & \cdots & \mathcal{P}_{N_r}^\nu(r_1) & \mathcal{N}^\nu(r_1, t_k) \\ \mathcal{P}_1^\nu(r_2) & \mathcal{P}_2^\nu(r_2) & \cdots & \mathcal{P}_{N_r}^\nu(r_2) & \mathcal{N}^\nu(r_2, t_k) \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ \mathcal{P}_1^\nu(r_{N_r}) & \mathcal{P}_2^\nu(r_{N_r}) & \cdots & \mathcal{P}_{N_r}^\nu(r_{N_r}) & \mathcal{N}^\nu(r_{N_r}, t_k) \end{bmatrix} \\ &\qquad \sim \begin{bmatrix} 1 & 0 & \cdots & 0 & v_1^\nu(t_{k+1/2}) \\ 0 & 1 & \cdots & 0 & v_2^\nu(t_{k+1/2}) \\ \vdots & \vdots & \ddots & \vdots & \vdots \\ 0 & 0 & \cdots & 1 & v_{N_r}^\nu(t_{k+1/2}) \end{bmatrix}. \end{aligned} \tag{2.98}$$

It is worthwhile to note that the augmented matrix is sparse, as is illustrated in Figure 5. This fact will be of some importance when choosing the computational method for Gauss-Jordan elimination. This same process should work in solving for the coefficients w_s^j.

$$\left[\begin{array}{ccccccccccccccc}
\mathcal{P}_1^\nu(r_1) & \mathcal{P}_2^\nu(r_1) & \mathcal{P}_3^\nu(r_1) & \mathcal{P}_4^\nu(r_1) & \mathcal{P}_5^\nu(r_1) & 0 & 0 & 0 & \cdots & 0 & 0 & 0 & 0 & \mathcal{N}^\nu(r_1,t_k) \\
\mathcal{P}_1^\nu(r_2) & \mathcal{P}_2^\nu(r_2) & \mathcal{P}_3^\nu(r_2) & \mathcal{P}_4^\nu(r_2) & \mathcal{P}_5^\nu(r_2) & 0 & 0 & 0 & \cdots & 0 & 0 & 0 & 0 & \mathcal{N}^\nu(r_2,t_k) \\
\mathcal{P}_1^\nu(r_3) & \mathcal{P}_2^\nu(r_3) & \mathcal{P}_3^\nu(r_3) & \mathcal{P}_4^\nu(r_3) & \mathcal{P}_5^\nu(r_3) & 0 & 0 & 0 & \cdots & 0 & 0 & 0 & 0 & \mathcal{N}^\nu(r_3,t_k) \\
0 & 0 & \mathcal{P}_3^\nu(r_4) & \mathcal{P}_4^\nu(r_4) & \mathcal{P}_5^\nu(r_4) & \mathcal{P}_6^\nu(r_4) & \mathcal{P}_7^\nu(r_4) & \mathcal{P}_8^\nu(r_4) & \cdots & 0 & 0 & 0 & 0 & \mathcal{N}^\nu(r_4,t_k) \\
0 & 0 & \mathcal{P}_3^\nu(r_5) & \mathcal{P}_4^\nu(r_5) & \mathcal{P}_5^\nu(r_5) & \mathcal{P}_6^\nu(r_5) & \mathcal{P}_7^\nu(r_5) & \mathcal{P}_8^\nu(r_5) & \cdots & 0 & 0 & 0 & 0 & \mathcal{N}^\nu(r_5,t_k) \\
0 & 0 & \mathcal{P}_3^\nu(r_6) & \mathcal{P}_4^\nu(r_6) & \mathcal{P}_5^\nu(r_6) & \mathcal{P}_6^\nu(r_6) & \mathcal{P}_7^\nu(r_6) & \mathcal{P}_8^\nu(r_6) & \cdots & 0 & 0 & 0 & 0 & \mathcal{N}^\nu(r_6,t_k) \\
0 & 0 & 0 & 0 & 0 & \mathcal{P}_6^\nu(r_7) & \mathcal{P}_7^\nu(r_7) & \mathcal{P}_8^\nu(r_7) & \cdots & 0 & 0 & 0 & 0 & \mathcal{N}^\nu(r_7,t_k) \\
0 & 0 & 0 & 0 & 0 & \mathcal{P}_6^\nu(r_8) & \mathcal{P}_7^\nu(r_8) & \mathcal{P}_8^\nu(r_8) & \cdots & 0 & 0 & 0 & 0 & \mathcal{N}^\nu(r_8,t_k) \\
0 & 0 & 0 & 0 & 0 & \mathcal{P}_6^\nu(r_9) & \mathcal{P}_7^\nu(r_9) & \mathcal{P}_8^\nu(r_9) & \cdots & 0 & 0 & 0 & 0 & \mathcal{N}^\nu(r_9,t_k) \\
\vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \vdots & \ddots & \vdots & \vdots & \vdots & \vdots & \vdots \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \cdots & \mathcal{P}_{N_r-3}^\nu(r_{N_r-5}) & \mathcal{P}_{N_r-2}^\nu(r_{N_r-5}) & \mathcal{P}_{N_r-1}^\nu(r_{N_r-5}) & 0 & \mathcal{N}^\nu(r_{N_r-5},t_k) \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \cdots & \mathcal{P}_{N_r-3}^\nu(r_{N_r-4}) & \mathcal{P}_{N_r-2}^\nu(r_{N_r-4}) & \mathcal{P}_{N_r-1}^\nu(r_{N_r-4}) & 0 & \mathcal{N}^\nu(r_{N_r-4},t_k) \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \cdots & \mathcal{P}_{N_r-3}^\nu(r_{N_r-3}) & \mathcal{P}_{N_r-2}^\nu(r_{N_r-3}) & \mathcal{P}_{N_r-1}^\nu(r_{N_r-3}) & 0 & \mathcal{N}^\nu(r_{N_r-3},t_k) \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \cdots & \mathcal{P}_{N_r-3}^\nu(r_{N_r-2}) & \mathcal{P}_{N_r-2}^\nu(r_{N_r-2}) & \mathcal{P}_{N_r-1}^\nu(r_{N_r-2}) & \mathcal{P}_{N_r}^\nu(r_{N_r-2}) & \mathcal{N}^\nu(r_{N_r-2},t_k) \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \cdots & \mathcal{P}_{N_r-3}^\nu(r_{N_r-1}) & \mathcal{P}_{N_r-2}^\nu(r_{N_r-1}) & \mathcal{P}_{N_r-1}^\nu(r_{N_r-1}) & \mathcal{P}_{N_r}^\nu(r_{N_r-1}) & \mathcal{N}^\nu(r_{N_r-1},t_k) \\
0 & 0 & 0 & 0 & 0 & 0 & 0 & 0 & \cdots & \mathcal{P}_{N_r-3}^\nu(r_{N_r}) & \mathcal{P}_{N_r-2}^\nu(r_{N_r}) & \mathcal{P}_{N_r-1}^\nu(r_{N_r}) & \mathcal{P}_{N_r}^\nu(r_{N_r}) & \mathcal{N}^\nu(r_{N_r},t_k)
\end{array}\right]$$

Figure 5: This is the augmented version of the P^ν matrix. The number of rows (N_r) indicates the number of collocation points that were chosen to give us enough equations to solve for the $3N_s-3$ spline coefficients ($N_r=3N_s-3$). The number of columns ($3N_s$–2) indicates the number of splines used, plus another column of complex numbers. Since there are three collocations points per two-node interval and each spline S_s (except for the end-splines) are considered as extending over three-node intervals, there are six nonzero entries per column. Since there are three splines per three-node interval (characterizing the values of the function and its first and second derivatives at the center node), there is a repeated three-column pattern in the placement of nonzero elements. The end-splines only cover one interval each; there are two splines associated with the origin and one spline associated with the extremal radial point.

Finally, we have determined how to solve for an approximate discrete time-evolved wavefunction, using splines and their coefficients in two representations. We may thus return to our original question: what is the probability $P_n(t)$ that the antihydrogen atom will be in a state with energy E_n at time t? We can answer this question now in terms of these coefficients. Here is a restatement of Equation 2.2 that is finally expressed in the spline coefficient representation of the solution wavefunction:

$$\begin{aligned}
P_n(t) &= \left| \left\langle \sum_{lm} \psi_{nlm}(\mathbf{r}) \middle| \Psi(\mathbf{r},t) \right\rangle \right|^2 \\
&= \left| \sum_{lm} \langle \psi_{nlm}(\mathbf{r}) | \Psi(\mathbf{r},t) \rangle \right|^2 \\
&= \left| \sum_{lm} \sum_{\nu} \langle R_{nl}(r) Y_{lm}(\Omega) | F_{\nu}(r,t)\, \Upsilon_{\nu}(\Omega) \rangle \right|^2 \\
&= \left| \sum_{lm} \sum_{\nu} \sum_{m'} \left\langle R_{nl}(r) Y_{lm}(\Omega) \middle| \frac{1}{r} V_{\nu}(r,t)\, O_{p_\nu m'}\, Y_{l_\nu m'}(\Omega) \right\rangle \right|^2 \\
&= \left| \sum_{lm} \sum_{\nu} \sum_{m'} \sum_{s} \left\langle R_{nl}(r) Y_{lm}(\Omega) \middle| \frac{1}{r} v_s^{\nu}(t)\, S_s(r)\, O_{p_\nu m'}\, Y_{l_\nu m'}(\Omega) \right\rangle \right|^2 \\
&= \left| \sum_{lm} \sum_{l_\nu p_\nu} \sum_{m'} \sum_{s} \left\langle R_{nl}(r) Y_{lm}(\Omega) \middle| \frac{1}{r} v_s^{l_\nu p_\nu}(t)\, S_s(r)\, O_{p_\nu m'}\, Y_{l_\nu m'}(\Omega) \right\rangle \right|^2 \\
&= \left| \sum_{lm} \sum_{l_\nu p_\nu} \sum_{m'} \sum_{s} \left\langle R_{nl}(r) \middle| \frac{1}{r} S_s(r) \right\rangle \langle Y_{lm}(\Omega) | Y_{l_\nu m'}(\Omega) \rangle\; v_s^{l_\nu p_\nu}(t)\, O_{p_\nu m'} \right|^2 \\
&= \left| \sum_{lm} \sum_{p_l} \sum_{s} \left\langle R_{nl}(r) \middle| \frac{1}{r} S_s(r) \right\rangle v_s^{lp_l}(t)\, O_{p_l m} \right|^2 \\
&= \left| \sum_{lm} \sum_{p_l} \sum_{s} \sum_{i} \omega_i\, R_{nl}(r_i)\, \frac{1}{r_i}\, S_s(r_i)\, v_s^{lp_l}(t)\, O_{p_l m} \right|^2 .
\end{aligned}$$

Similarly, Equation 2.3 is restated as

$$P_{nl}(t) = \left| \sum_{m} \sum_{p_l} \sum_{s} \sum_{i} \omega_i\, R_{nl}(r_i)\, \frac{1}{r_i}\, S_s(r_i)\, v_s^{lp_l}(t)\, O_{p_l m} \right|^2 . \tag{2.99}$$

To be blunt, that concludes the explication of our mathematical approach.

2.3 Condensed Review

With such a long and involved explanation of our approach, it would be nice to restate the important parts concisely, so as to obtain a good over-all perspective. Here we go, then.

We started with the question of finding the time-dependent probability of an antihydrogen atom being in a particular energy eigenstate. Thus, we had to solve the time-dependent Shroödinger equation for this situation. As the problem was not ammenable to analytic solution, we disretized time and used an approximation of the propagator; we used a two-step propagation method, as described by Marchuk [1]. At this point we had Equations 2.20 and 2.21:

$$\left(1+i\frac{\Delta t}{2\hbar}\hat{H}_0(\mathbf{r})\right)\Psi(\mathbf{r},t_{k+1/2})=\left(1-i\frac{\Delta t}{2\hbar}\hat{H}_0(\mathbf{r})\right)\Psi(\mathbf{r},t_k), \tag{2.100}$$

a differential equation, and

$$\left(1+i\frac{\Delta t}{2\hbar}\hat{h}(\mathbf{r},t_k)\right)\Psi(\mathbf{r},t_{k+1})=\left(1-i\frac{\Delta t}{2\hbar}\hat{h}(\mathbf{r},t_k)\right)\Psi(\mathbf{r},t_{k+1/2}), \tag{2.101}$$

a linear equation. Since each of these equations is most simply handled in a different representation, we developed our method of representation in momentum- and coordinate-space and found an invertible transformation that could move us between the representations. In this development, we discretized the angular coordinates and chose which N momenta states and N angular points would take precedence. We then had $\widetilde{\Psi}^M_\nu = F_\nu$, $\widetilde{\Psi}^C_j = G_j$, and $\widetilde{\Psi}^M = Q\,\widetilde{\Psi}^C$.

Our next step was in analogy with the free-space hydrogen problem; we multiplied our latest versions of Equations 2.100 and 2.101 by r, which gave us a more simple version of the differential equation (Equation 2.100) with $\widetilde{\mathcal{U}}^M = r\widetilde{\Psi}^M$, $\widetilde{\mathcal{U}}^C = r\widetilde{\Psi}^C$, and $\widetilde{\mathcal{U}}^M = Q\widetilde{\mathcal{U}}^C$. We also let $\widetilde{\mathcal{U}}^M_\nu = V_\nu$ and $\widetilde{\mathcal{U}}^C_j = W_j$. Then, since we knew we would be using computers to solve our equations for us, we used spline approximations of $\mathcal{U}$ in both representations to turn the differential equation into a linear equation. Using quintic splines with N_s nodes, that left us with $N_r = 3N_s - 3$ splines, considering the boundary conditions. The time-dependent spline coefficients were called v^ν_s and w^j_s, and the transformation between the two representations remained the same: $v(t) = Q\,w(t)$, or

$$\begin{bmatrix} v^1_1(t) & v^1_2(t) & \cdots & v^1_{N_r}(t) \\ v^2_1(t) & v^2_2(t) & \cdots & v^2_{N_r}(t) \\ \vdots & \vdots & \ddots & \vdots \\ v^N_1(t) & v^N_2(t) & \cdots & v^N_{N_r}(t) \end{bmatrix} = Q \begin{bmatrix} w^1_1(t) & w^1_2(t) & \cdots & w^1_{N_r}(t) \\ w^2_1(t) & w^2_2(t) & \cdots & w^2_{N_r}(t) \\ \vdots & \vdots & \ddots & \vdots \\ w^N_1(t) & w^N_2(t) & \cdots & w^N_{N_r}(t) \end{bmatrix}, \tag{2.102}$$

so long as we ensured that $N = N_r$. To be able to solve each linear equation for all of the N^2 spline coefficients, we picked N_r collocation points to give us a system of discrete equations with the same number of equations as unknowns. At this point we had

$$\mathcal{P}^\nu\, v^\nu(t_{k+1/2}) = \mathcal{M}^\nu\, v^\nu(t_k) \tag{2.103}$$

and

$$\mathcal{P}^j(t_k)\, w^j(t_{k+1}) = \mathcal{M}^j(t_k)\, w^j(t_{k+1/2}). \tag{2.104}$$

Showing the matrices explicitly and simplifying the right-hand side, we represented these

Step	Input	Perform this task...	Output
1	$w(t_0)$	Multiply: $Q\,w(t_0)$	$v(t_0)$
2	$v(t_0)$	Solve $\mathcal{P}^\nu\, v^\nu(t_{1/2}) = \mathcal{M}^\nu\, v^\nu(t_0)$ for each ν	$v(t_{1/2})$
3	$v(t_{1/2})$	Multiply: $Q^{-1}\, v(t_{1/2})$	$w(t_{1/2})$
4	$w(t_{1/2})$	Solve $\mathcal{P}^j(t_0)\, w^j(t_1) = \mathcal{M}^j(t_0)\, w^j(t_{1/2})$ for each j	$w(t_1)$
5	$w(t_1)$	Multiply: $Q\,w(t_1)$	$v(t_1)$
6	$v(t_1)$	Solve $\mathcal{P}^\nu\, v^\nu(t_{3/2}) = \mathcal{M}^\nu\, v^\nu(t_1)$ for each ν	$v(t_{3/2})$
7	$v(t_{3/2})$	Multiply: $Q^{-1}\, v(t_{3/2})$	$w(t_{3/2})$
8	$w(t_{3/2})$	Solve $\mathcal{P}^j(t_1)\, w^j(t_2) = \mathcal{M}^j(t_1)\, w^j(t_{3/2})$ for each j	$w(t_2)$
$\vdots$	$\vdots$	$\vdots$	$\vdots$
4k+1	$w(t_k)$	Multiply: $Q\,w(t_k)$	$v(t_k)$
4k+2	$v(t_k)$	Solve $\mathcal{P}^\nu\, v^\nu(t_{k+1/2}) = \mathcal{M}^\nu\, v^\nu(t_k)$ for each ν	$v(t_{k+1/2})$
4k+3	$v(t_{k+1/2})$	Multiply: $Q^{-1}\, v(t_{k+1/2})$	$w(t_{k+1/2})$
4k+4	$w(t_{k+1/2})$	Solve $\mathcal{P}^j(t_k)\, w^j(t_{k+1}) = \mathcal{M}^j(t_k)\, w^j(t_{k+1/2})$ for each j	$w(t_{k+1})$
$\vdots$	$\vdots$	$\vdots$	$\vdots$

Table 1: Steps for Time-Propagation of the Wavefunction

equations like so:

$$\begin{bmatrix} \mathcal{P}_1^\nu(r_1) & \mathcal{P}_2^\nu(r_1) & \cdots & \mathcal{P}_{N_r}^\nu(r_1) \\ \mathcal{P}_1^\nu(r_2) & \mathcal{P}_2^\nu(r_2) & \cdots & \mathcal{P}_{N_r}^\nu(r_2) \\ \vdots & \vdots & \ddots & \vdots \\ \mathcal{P}_1^\nu(r_{N_r}) & \mathcal{P}_2^\nu(r_{N_r}) & \cdots & \mathcal{P}_{N_r}^\nu(r_{N_r}) \end{bmatrix} \begin{bmatrix} v_1^\nu(t_{k+1/2}) \\ v_2^\nu(t_{k+1/2}) \\ \vdots \\ v_{N_r}^\nu(t_{k+1/2}) \end{bmatrix} = \begin{bmatrix} \mathcal{N}^\nu(r_1,t_k) \\ \mathcal{N}^\nu(r_2,t_k) \\ \vdots \\ \mathcal{N}^\nu(r_{N_r},t_k) \end{bmatrix} \tag{2.105}$$

and

$$\begin{bmatrix} \mathcal{P}_1^j(r_1,t_k) & \mathcal{P}_2^j(r_1,t_k) & \cdots & \mathcal{P}_{N_r}^j(r_1,t_k) \\ \mathcal{P}_1^j(r_2,t_k) & \mathcal{P}_2^j(r_2,t_k) & \cdots & \mathcal{P}_{N_r}^j(r_2,t_k) \\ \vdots & \vdots & \ddots & \vdots \\ \mathcal{P}_1^j(r_{N_r},t_k) & \mathcal{P}_2^j(r_{N_r},t_k) & \cdots & \mathcal{P}_{N_r}^j(r_{N_r},t_k) \end{bmatrix} \begin{bmatrix} w_1^j(t_{k+1}) \\ w_2^j(t_{k+1}) \\ \vdots \\ w_{N_r}^j(t_{k+1}) \end{bmatrix} = \begin{bmatrix} \mathcal{N}^j(r_1,t_{k+1/2}) \\ \mathcal{N}^j(r_2,t_{k+1/2}) \\ \vdots \\ \mathcal{N}^j(r_{N_r},t_{k+1/2}) \end{bmatrix}. \tag{2.106}$$

At this point we had figured out how to calculate an approximate solution of Schrödinger's equation using a two-step propagation. So starting at $t_0 = 0$ with an initial antihydrogen wavefunction, represented as a matrix of spline coefficients $w(t_0)$, we may now use a computer program to propagate the wavefunction into the future using the steps shown in Table 1. After following these steps, we will know $v_s^{lp_l}(t_k)$ for all times t_k that interest us, and we can finally calculate the probability of an antihydrogen atom being in a particular R_{nl} state:

$$P_{nl}(t_k) = \left| \sum_{m=-l}^{l} \sum_{p_l=0}^{2l} \sum_{s=1}^{N_r} \sum_{i=1}^{N_r} \omega_i\, R_{nl}(r_i)\, \frac{S_s(r_i)}{r_i}\, O_{p_l m}\, v_s^{lp_l}(t_k) \right|^2. \tag{2.107}$$

3 Computational Work

David Caballero wrote a computer program in the C programming language to propagate discretized antihydrogen-in-a-laser-field wavefunctions over time and calculate the probabilities at each time interval of the atom occupying certain states. The workings of the program and its initial results are discussed in the following sections.

3.1 Program Description

The basic function of the program is to perform the steps listed previously in Table 1, then calculate probabilities using Equation 2.107. It also calculates the inner product of the wavefunction with itself $\langle\Psi|\Psi\rangle$ to allow us to see how well the wavefunction remains normalized, and it calculates the average energy $\langle E\rangle$ of the antihydrogen atom and $\langle E-h\rangle$. We must provide the program several sets of data before it can do its job, though. First of all, we must choose how we will discretize the wavefunction. Depending on the computational power of the computer on which the program is running, and depending on how long we are willing to wait for the results, we have to determine: the number N_s of radial spline nodes and thus the number $N = N_r = 3N_s - 3$ of discrete momentum states, angular points, and radial collocation points; the size of the time interval Δt; and the number of iterations the program should perform before it stops. The number N determines the range of the indices ν, j, and i, and the number of iterations determines the range of the index k. We must also decide where the spline nodes should be located and which momentum states will take precedence[10]. Once these decisions are made, the constants O_{pm} are determined by Gram-Schmidt orthonormalization, and the location of the collocation points, the location of the angular points, and the weights w_j and w_i are determined by Gaussian quadrature rules. Finally, we must supply an initial normalized wavefunction $\Psi_{initial}$ and choose the R_{nl} states for which we want to find probabilities. The initial wavefunction may just as well be one of the R_{nl} states, but whatever function we pick, we must know what its first and second derivatives are so that we can calculate its spline representation $w(t_0)$. With all of these decisions made, the program is free to calculate.

One matter about the method of calculation deserves further discussion, and that is the solution of the matrix equations. Since $\mathcal{P}^j(t_k)$ is time-dependent, it must be calculated for each moment in time. If the period of $\hat{h}(r,t)$ is divisible by Δt, then there will be some repitition of $\mathcal{P}^j(t_k)$ over time. Since $\mathcal{P}^\nu$ is not time-dependent, it only needs to be calculated once and used repeatedly. For all of these cases where we want to solve matrix equations of the form $A\mathbf{x} = \mathbf{b}$ for multiple $\mathbf{b}$ vectors and the same matrix A, it is most efficient to use LU factorization. If we factor A into a product of a permuted lower triangular matrix L and an upper triangular matrix U, which is the echelon form of A, then the process of solving $A\mathbf{x} = LU\mathbf{x} = \mathbf{b}$ can be broken into the more managable processes of solving $L\mathbf{y} = \mathbf{b}$ and then $U\mathbf{x} = \mathbf{y}$. We take advantage of this technique by using either LAPACK (Linear Algebra PACKage) or SuperLU, a program designed for sparse Gaussian elimination on high

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[10] One general method of picking momentum states was discussed immediately before Equation 2.54, and that is the method used in our recent run of the program that produced the results included here. We will not discuss the method used for selecting the spline nodes. Suffice it to say that it takes a certain amount of experience to hand-pick the appropriate points.

performance computers.

The other feature of the program that is worth mentioning is that it may be run in a parallel mode, where separate calculations are assigned to different processors. This is due to the fact that each time a set of matrix equations are solved, whether it be solving N equations of the form $\mathcal{P}^\nu\, v^\nu(t_{k+1/2}) = \mathcal{M}^\nu\, v^\nu(t_k)$ or N equations of the form $\mathcal{P}^j(t_k)\, w^j(t_{k+1}) = \mathcal{M}^j(t_k)\, w^j(t_{k+1/2})$, the set of N equations are independent. Thus, we may write code that is, as they say, "embarrassingly parallel" to solve this problem. The rest of the details about how the program was written and is organized are beyond the scope of this paper.

3.2 Results

We ran our code on a supercomputer called DataStar at the San Diego Supercomputing Center at the University of California, San Diego and on an SGI computer called Atlantis here at California State University, Long Beach. Personally, I was not able to run the program on DataStar, but I was able to run it in serial mode on Atlantis. The resulting data is included here from the runs I made on Atlantis. The initial state of the antihydrogen atom is the $3s$ state, where $n=3$ and $l=0$.

Iteration	**Time (atu)**	$\langle \Psi \vert \Psi \rangle$	$P_{3,0} = \vert \langle \Psi \vert \Psi_{initial} \rangle \vert^2$	$P_{1,0} = \vert \langle \Psi \vert 1s \rangle \vert^2$	$P_{2,0} = \vert \langle \Psi \vert 2s \rangle \vert^2$
1	0.2824	1.0000000001600435	1.0000000000438676	6.9210938639514229e-11	3.0749096466587819e-11
10,000	1412.14	0.99999984397683239	0.99730264647522737	2.8990034021170673e-08	1.2229594963067767e-06
20,000	2824.14	0.99999996338419372	0.99956169618506296	6.8185178346502936e-08	6.0631182055602294e-07
30,000	4236.14	0.9999998664145997	0.99764679542926882	5.2625377303866976e-08	5.3017415127935915e-07
40,000	5648.14	0.99999986132807839	0.99876098684541892	8.4155120441696719e-09	1.6097558975076965e-06
50,000	7060.14	0.9999999031016189	0.99807732283024442	8.0267177415140301e-09	5.8034906145707176e-08
60,000	8472.14	0.99999977514256755	0.99826257539317753	5.2486253523814282e-08	1.6530061835498476e-06
70,000	9884.14	1.0000000005448675	0.99838957868162004	6.8027569042587192e-08	4.0301109198219256e-07
80,000	11296.1	0.99999980722273996	0.99810196451366184	2.9585147866093131e-08	6.7294896182846354e-07
90,000	12708.1	0.99999998564158443	0.99841849557861451	3.8721480763704593e-12	1.1420415109022723e-06
100,000	14120.1	0.99999985790725199	0.99824101968346957	2.822486613149762e-08	2.4603051681596989e-09
110,000	15532.1	0.99999994076868615	0.99800714470594898	6.8237222869642138e-08	1.3360556252437067e-06
120,000	16944.1	0.99999995289432486	0.9987183832592279	5.362564170013796e-08	5.4362927234720141e-07
130,000	18356.1	0.9999998432434577	0.99731019157380518	8.6536153000526723e-09	7.1760473924611183e-07
140,000	19768.1	0.9999999930543344	0.99914869721048472	7.6144643428316341e-09	1.5477581194716428e-06
150,000	21180.1	0.99999973435518164	0.99684851679539388	5.2133988231942534e-08	8.4488537996544332e-08

Table 2: This is the first of two tables that contain data for an antihydrogen atom starting in the $3s$ state. The data includes the normalization of the wavefunction, transition probabilites to lower energy states and back to the original state, and average energies (in the next table). The times in the second column are in atomic time units (atu), where one atu equals 2.418884×10^{-17} seconds. The value of one atu in terms of seconds is the same as the value of the reduced Planck's constant $\hbar$ in terms of Hartree-seconds, where a Hartree E_h is a unit of energy given by $E_h = \hbar^2/m_e a_0^2$.

Iteration	**Time (atu)**	$P_{2,1} = \lvert \langle \Psi \vert 2p \rangle \rvert^2$	$\langle E - h \rangle$	$\langle E \rangle$
1	0.2824	0.0042467120211789723	-0.055525299063669153	-0.055525299063669153
10,000	1412.14	0.0043329880708483899	-0.055322682187297752	-0.055322749083048052
20,000	2824.14	0.0042739941932816387	-0.055493754090326489	-0.055493882662816608
30,000	4236.14	0.0042453723080727607	-0.055346643227296266	-0.055347247070501301
40,000	5648.14	0.0043655394959590263	-0.055427854667047409	-0.055428021997688696
50,000	7060.14	0.0041994621575397731	-0.055368554166993891	-0.055369751491163174
60,000	8472.14	0.0043608228518586993	-0.055389651382419483	-0.055390082891782211
70,000	9884.14	0.0042351100052539373	-0.055395342061034393	-0.055396435958346847
80,000	11296.1	0.0042863156813478503	-0.055363496788519165	-0.055364787665946789
90,000	12708.1	0.0043462310047777727	-0.055395775431166576	-0.055395912798885727
100,000	14120.1	0.0042222634106653745	-0.055346940794936066	-0.055347921650238781
110,000	15532.1	0.0043449687929037126	-0.055357207538570131	-0.055355956238290503
120,000	16944.1	0.0042529213066699427	-0.055386150273767552	-0.055385910559826217
130,000	18356.1	0.0042760011264214833	-0.055292283993705935	-0.055289441417259985
140,000	19768.1	0.0043540682203416382	-0.055413725220961309	-0.055413093031157115
150,000	21180.1	0.0041937725553593749	-0.055246323778901436	-0.055242100788608146

Table 3: This is the second of two tables that contain data for an antihydrogen atom starting in the 3s state.

3.3 Analysis

The first thing to notice about the data is that the number of iterations is relatively small. Although 150,000 iterations may seem large, given our time step of 0.2824 atomic time units (atu) that only translates to a duration of about 21,000 atu, or one-half of a picosecond. On later runs, we would like time scales of a few orders of magnitude larger. Secondly, we should note that the wavefunction does remain approximately normalized, as it should. However, the total probability of the atom occupying any one state is greater than one, or more significantly, greater than $\langle\Psi|\Psi\rangle$. For instance, at $t = 21180.1$ atu, $\langle\Psi|\Psi\rangle = 0.9999997$, but the sum of the probability that the atom is in the $3s$ state (0.9968485) and the probability that the atom is in the $2p$ state (0.0041938) is 1.0010423. Even so, a comparison of the individual probabilities makes sense. The wavefunction has a high probability of remaining in its initial state of $3s$ up to this point in the simulation. The situation is that the atom starts in a state where $l = 0$, and it interacts with a photon of spin 1. The data shows that if the atom does make a transition to a state of lower energy, it is much more likely to end up in a state with $l = 1$ than a state with $l = 0$. The probability of the atom transitioning to the $2p$ state remains at about 0.0043, which is several orders of magnitude larger than the probability of the atom occupying the $2s$ state (about 10^{-7}) or the $1s$ state (about 10^{-9}). Of course, the probabilities also drop off more for states that have energies that are further away from the original energy: when the atom starts from an $n = 3$ state, it is more likely that it transitions to an $n = 2$ state than an $n = 1$ state. We need to do a more thorough analysis, starting with a higher initial energy state and examining more transitions, to determine what the larger, more predominant patterns are.

4 Conclusion

Before the full value of the techniques presented in this paper can be realized, and before new insight can be provided by the resulting data, there must be a more thorough analysis of transition probabilities. This run of the program was really a preliminary run for a more in-depth investigation requiring many runs of the program with initial states approaching $n = 50$ and having various angular momenta. After this kind of investigation is done, there will be more information with which to justify moving on to the three-body scattering problem that was mentioned in the introduction.

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6 Appendices

A Hydrogen Atom Solution

The solution of the wavefunction for a hydrogen atom in free space is important to our solution of the wavefunction for an antihydrogen atom in a laser field. Specifically, it is important because we want to use the energy eigenstates found in the hydrogen atom solution to find the probability that the antihydrogen atom is in one of these states. In this appendix we derive the solution for the hydrogen atom. We assume that we have an electron and a proton together in empty, three-dimensional space. The electron has mass m and charge $-e$, and the proton has mass M and charge e. There is no laser field in this problem, as there is in our antihydrogen problem.

A.1 Center-of-Mass Coordinate Change

From classical mechanics, we are familiar with the fact that, in any inertial reference frame, the dynamics of an isolated system of two charged point-particles may be described in terms of the individual particles' masses, charges, positions, and momenta or in terms of a "center-of-mass particle" and a "reduced-mass particle" and their associated properties. These mathematically constructed particles arise from a mere change of variables (and masses): given that particle 1 has mass m_1, charge q_1, position $\mathbf{r}_1$ with respect to an "observing" reference frame, and momentum $\mathbf{p}_1$, and given that particle 2 has mass m_2, charge q_2, position $\mathbf{r}_2$ with respect to the same frame, and momentum $\mathbf{p}_2$, we let $\mathbf{R} = (m_1\mathbf{r}_1 + m_2\mathbf{r}_2)/(m_1 + m_2)$, $M = m_1 + m_2$, $\mathbf{r} = \mathbf{r}_1 - \mathbf{r}_2$, and $1/\mu = 1/m_1 + 1/m_2$. Since $\mathbf{p}_1 = m_1\dot{\mathbf{r}_1}$ and $\mathbf{p}_2 = m_2\dot{\mathbf{r}_2}$, $\mathbf{p}_1$ and $\mathbf{p}_2$ transform in a similar manner as $\mathbf{r}_1$ and $\mathbf{r}_2$ so that $\mathbf{P} = M\dot{\mathbf{R}}$ and $\mathbf{p} = \mu\dot{\mathbf{r}}$. Thus the Hamiltonian transforms from

$$H(\mathbf{r}_1, \mathbf{r}_2, \mathbf{p}_1, \mathbf{p}_2) = \frac{|\mathbf{p}_1|^2}{2m_1} + \frac{|\mathbf{p}_2|^2}{2m_2} - \kappa\frac{q_1 q_2}{|\mathbf{r}_1 - \mathbf{r}_2|} \tag{A.1}$$

to

$$H(\mathbf{R}, \mathbf{r}, \mathbf{P}, \mathbf{p}) = \frac{|\mathbf{P}|^2}{2M} + \frac{|\mathbf{p}|^2}{2\mu} - \kappa\frac{q_1 q_2}{|\mathbf{r}|}. \tag{A.2}$$

So, after the change of variables, we have a Hamiltonian that seems to be describing one free particle at the center of mass $\mathbf{R}$ with mass M and momentum $\mathbf{P}$ and another particle at the "relative" coordinate $\mathbf{r}$ with mass μ, called the reduced mass, and momentum $\mathbf{p}$ that is affected by a central force proportional to $q_1 q_2$. The vector $\mathbf{R}$ is defined with respect to the lab frame, but the vector $\mathbf{r}$ is defined with respect to a "relative" frame that has its origin located at particle 2. Since particle 2 accelerates with respect to the center of mass, the relative frame accelerates with respect to the observing frame; thus the relative frame is not inertial. This doesn't matter, though, since we already know that our equations are true. We shall call the vector space of coordinates associated with the observing frame $\mathbf{R}$-space (or $\mathbf{r}_1$-space or $\mathbf{r}_2$-space) and we shall call the space associated with the relative frame $\mathbf{r}$-space.

Anyway, since the new Hamiltonian in Equation A.2 can be expressed as a sum of two Hamiltonians, one that characterizes the center-of-mass particle and one that characterizes the reduced-mass particle, Hamilton's equations determine that these particles do not interact with each other. Instead, they behave independently of each other as if they were in different superimposed universes. The center-of-mass particle moves with constant momentum and the reduced-mass particle follows some conic-section trajectory about the tail of the $\mathbf{r}$ vector. Translating these trajectories back to the trajectories of the real particles is simple: $\mathbf{r}_1 = \mathbf{R} + m_2\mathbf{r}/(m_1+m_2)$ and $\mathbf{r}_2 = \mathbf{R} - m_1\mathbf{r}/(m_1+m_2)$. We must realize, though, that the momentum of the center-of-mass particle may take any classically possible value and that the coordinate system of the vector $\mathbf{r}$ may be oriented in any manner with respect to the coordinate system of vector $\mathbf{R}$.

In the quantum mechanical two-body problem we may perform the same change of variables, except in this case it is also a change of operators. The vectors $\mathbf{r}_1$ and $\mathbf{r}_2$ no longer represent the positions of the particles but instead act as eigenstates ($|\mathbf{r}_1\rangle$ and $|\mathbf{r}_2\rangle$) and operators ($\hat{\mathbf{r}}_1$ and $\hat{\mathbf{r}}_2$) for position in coordinate space. The dynamics of the two particles are no longer specified by curves in coordinate space (or configuration space or phase space) but they are specified by a state vector $|\Psi(t)\rangle$ in a Hilbert space. The position operators $\hat{\mathbf{r}}_1$ and $\hat{\mathbf{r}}_2$ and the momentum operators $\hat{\mathbf{p}}_1$ and $\hat{\mathbf{p}}_2$ act on state vectors in the given Hilbert space. The change of operators takes the Hamiltonian to the same form as before:

$$\hat{H}(\hat{\mathbf{R}}, \hat{\mathbf{r}}, \hat{\mathbf{P}}, \hat{\mathbf{p}}) = \frac{|\hat{\mathbf{P}}|^2}{2M} + \frac{|\hat{\mathbf{p}}|^2}{2\mu} - \kappa\frac{q_1 q_2}{|\hat{\mathbf{r}}|}. \tag{A.3}$$

Again, the Hamiltonian may be written as a sum of two particle-specific Hamiltonians: $\hat{H}(\hat{\mathbf{R}}, \hat{\mathbf{r}}, \hat{\mathbf{P}}, \hat{\mathbf{p}}) = \hat{H}_R(\hat{\mathbf{R}}, \hat{\mathbf{P}}) + \hat{H}_r(\hat{\mathbf{r}}, \hat{\mathbf{p}})$. Picking a particular representation, say the representation with respect to the coordinate basis $|\mathbf{R}, \mathbf{r}\rangle$, gives us this Hamiltonian:

$$\hat{H}(\mathbf{R}, \mathbf{r}) = \left\langle \mathbf{R}, \mathbf{r} \middle| \hat{H} \middle| \mathbf{R}, \mathbf{r} \right\rangle = -\frac{\hbar^2 {\nabla_{\mathbf{R}}}^2}{2M} - \frac{\hbar^2 {\nabla_{\mathbf{r}}}^2}{2\mu} - \kappa\frac{q_1 q_2}{|\mathbf{r}|}, \tag{A.4}$$

where the laplacian ${\nabla_{\mathbf{R}}}^2$ differentiates with respect to coordinates in $\mathbf{R}$-space and similarly for ${\nabla_{\mathbf{r}}}^2$. Of course, the wavefunction for the two particles, expressed in the coordinate space basis, changes from $\Psi(\mathbf{r}_1, \mathbf{r}_2, t)$ to $\Psi(\mathbf{R}, \mathbf{r}, t)$. Solving Schrödinger's equation in this new basis,

$$\hat{H}(\mathbf{R}, \mathbf{r})\, \Psi(\mathbf{R}, \mathbf{r}, t) = i\hbar\frac{\partial}{\partial t}\, \Psi(\mathbf{R}, \mathbf{r}, t), \tag{A.5}$$

enables us to use the technique of separation of variables, where $\Psi(\mathbf{R}, \mathbf{r}, t) = \chi(\mathbf{R})\, \psi(\mathbf{r})\, \tau(t)$. We shall call χ the center-of-mass wavefunction, ψ the relative wavefunction, and τ the time wavefunction. With separated variables, we may rearrange the equation: if

$$\left[\hat{H}_R(\mathbf{R}) + \hat{H}_r(\mathbf{r})\right] \chi(\mathbf{R})\psi(\mathbf{r})\tau(t) = \hat{E}\, \chi(\mathbf{R})\psi(\mathbf{r})\tau(t),$$

then functions unaffected by certain operators may commute with those certain operators like so,

$$\psi(\mathbf{r})\tau(t)\, \hat{H}_R(\mathbf{R})\, \chi(\mathbf{R}) + \chi(\mathbf{R})\tau(t)\, \hat{H}_r(\mathbf{r})\, \psi(\mathbf{r}) = \chi(\mathbf{R})\psi(\mathbf{r})\, \hat{E}\, \tau(t),$$

and if we divide by $\chi(\mathbf{R})\, \psi(\mathbf{r})\, \tau(t)$, then we have

$$\frac{1}{\chi(\mathbf{R})}\hat{H}_R(\mathbf{R})\, \chi(\mathbf{R}) + \frac{1}{\psi(\mathbf{r})}\hat{H}_r(\mathbf{r})\, \psi(\mathbf{r}) = \frac{1}{\tau(t)}\hat{E}\, \tau(t).$$

Since $\mathbf{R}$, $\mathbf{r}$, and t are independent variables and are separated into individual terms, varying one of them at a time will not affect the value the other two terms; so each term must equal a constant. That implies that each of the wavefunctions are energy eigenstates. Let's call the eigenvalues of χ, ψ, and τ E_R, E_r, and E_t, respectively. Then $E_t = E_R + E_r$ and we have three resulting equations:

$$\hat{H}_R(\mathbf{R})\,\chi(\mathbf{R}) = -\tfrac{\hbar^2\nabla^2}{2M}\,\chi(\mathbf{R}) = E_R\,\chi(\mathbf{R}) \tag{A.6}$$

$$\hat{H}_r(\mathbf{r})\,\psi(\mathbf{r}) = \left[-\tfrac{\hbar^2\nabla^2}{2\mu} - \kappa\tfrac{q_1q_2}{r}\right]\psi(\mathbf{r}) = E_r\,\psi(\mathbf{r}) \tag{A.7}$$

$$\hat{E}\,\tau(t) = i\hbar\tfrac{\partial}{\partial t}\,\tau(t) = E_t\,\tau(t). \tag{A.8}$$

The solutions of Equations A.6 and A.8 should be familiar to us:

$$\chi(\mathbf{R}) = (2\pi)^{-3/2}e^{i\mathbf{P}\cdot\mathbf{R}\hbar}, \tag{A.9}$$

where $\mathbf{P}$ is any momentum vector such that $P^2/2M = E_R$, and

$$\tau(t) = e^{-iE_tt/\hbar}. \tag{A.10}$$

Since $E_t = E_R + E_r$, τ may be expressed as the product two exponentials $\tau_R(t) = \exp(iE_Rt/\hbar)$ and $\tau_r(t) = \exp(iE_rt/\hbar)$, each of which may naturally couple by multiplication with their respective coordinate wavefunctions. So the three equations are essentially two independent time-dependent Schrödinger equations - one for each particle. The center-of-mass wavefunction has been given the coefficient $(2\pi)^{-3/2}$ so that its Fourier transformations are symmetrical:

$$\chi(\mathbf{P}) = (2\pi)^{-3/2}\int_{\mathbf{R}}\chi(\mathbf{R})\,e^{-i\mathbf{P}\cdot\mathbf{R}/\hbar}\,d\mathbf{R},$$

$$\chi(\mathbf{R}) = (2\pi)^{-3/2}\int_{\mathbf{P}}\chi(\mathbf{P})\,e^{i\mathbf{P}\cdot\mathbf{R}/\hbar}\,d\mathbf{P}.$$

The time wavefunction has been normalized with a coefficient of unity for the sake of simplicity. With these solutions, however, the overall wavefuncion Ψ cannot be normalized:

$$\begin{aligned}
\langle\Psi|\Psi\rangle &= \int_{all\ \mathbf{R}}\int_{all\ \mathbf{r}}|\Psi(\mathbf{R},\mathbf{r},t)|^2\,d\mathbf{R}\,d\mathbf{r} \\
&= \int_{all\ \mathbf{R}}\int_{all\ \mathbf{r}}|\chi(\mathbf{R})|^2\,|\psi(\mathbf{r})|^2\,|\tau(t)|^2\,d\mathbf{R}\,d\mathbf{r} \\
&= |\tau(t)|^2\int_{all\ \mathbf{R}}|\chi(\mathbf{R})|^2\,d\mathbf{R}\int_{all\ \mathbf{r}}|\psi(\mathbf{r})|^2\,d\mathbf{r} \\
&= 1\int_{all\ \mathbf{R}}\frac{1}{2\pi}\,d\mathbf{R}\int_{all\ \mathbf{r}}|\psi(\mathbf{r})|^2\,d\mathbf{r} \\
&= \infty\int_{all\ \mathbf{r}}|\psi(\mathbf{r})|^2\,d\mathbf{r}
\end{aligned}$$

Since there's a nonzero probability of finding the center-of-mass at every point in $\mathbf{R}$-space, the integral of $|\chi|^2$ diverges; thus we cannot meaningfully ask questions about where the center-of-mass particle *or* the reduced-mass particle are located. We can, however, ask about probabilities associated with energy states and momentum states.

If we make the assumption that the center of mass behaves classically, like a point particle compared to the reduced mass particle, then integrating $|\psi|^2$, where ψ is normalized, does relate to the position of the reduced mass particle with respect to the center of mass and thus it relates to the positions of the two original particles with respect to the center of mass. As in the classical case, the momentum of the center-of-mass particle may take any possible value and that the coordinate system of the vector $\mathbf{r}$ may be oriented in any manner with respect to the coordinate system of vector $\mathbf{R}$. This assumption of classical behavior of the center of mass is approximately true in the case where the two original particles are a proton and an electron. Since the proton is about 2000 times more massive than the electron, it is essentially immobile in the center-of-mass frame, and the center of mass is located approximately at the same position as the proton. We will not concern ourselves with the positions of the particles and how accurate this approximation is, but we will normalize ψ. Now all that remains is to solve Equation A.7 for the relative wavefunction ψ.

A.2 The Relative Wavefunction

Since the potential of H_r is spherically symmetric, we will work in spherical coordinates, where the Hamiltonian H_r takes the form

$$\begin{aligned}\hat{H}_r(\mathbf{r}) &= -\frac{\hbar^2}{2\mu}\nabla^2 - \kappa\frac{e^2}{r}\\ &= -\frac{\hbar^2}{2\mu}\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\left(\frac{\partial^2}{\partial \theta^2} + \frac{\cos\theta}{\sin\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right)\right] - \kappa\frac{e^2}{r},\end{aligned}$$

where θ is the polar angle measured from the z-axis ranging from 0 to π and ϕ is the azimuthal angle in the xy-plane ranging from 0 to 2π. Since

$$\hat{L}^2 = -\hbar^2\left(\frac{\partial^2}{\partial \theta^2} + \frac{\cos\theta}{\sin\theta}\frac{\partial}{\partial\theta} + \frac{1}{\sin^2\theta}\frac{\partial^2}{\partial\phi^2}\right), \tag{A.11}$$

we can simplify H_r further:

$$\begin{aligned}\hat{H}_r(\mathbf{r}) &= -\frac{\hbar^2}{2\mu}\left[\frac{\partial^2}{\partial r^2} + \frac{2}{r}\frac{\partial}{\partial r} + \frac{1}{r^2}\left(-\frac{\hat{L}^2}{\hbar^2}\right)\right] - \kappa\frac{e^2}{r}\\ &= -\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2} - \frac{\hbar^2}{\mu r}\frac{\partial}{\partial r} + \frac{\hat{L}^2}{2\mu r^2} - \kappa\frac{e^2}{r}. \qquad (A.12)\end{aligned}$$

We may now solve Equation A.7 for the relative wavefunction ψ in spherical coordinates. To simplify notation, we will let $E_r = E$. To keep track of the constants and quantities that characterize the solutions, we will add subscripts of these constants to the functions; so we have ψ_E.

We may employ the separation of variables technique and separate ψ_E into a product of functions of the radial and the angular coordinates. So, let

$$\psi_E(\mathbf{r}) = R(r)\,Y(\Omega), \tag{A.13}$$

where Ω represents both θ and ϕ. So far, we don't know if both R and Y depend upon E or if only one of them does, so we'll leave the subscripts undetermined for now. Since $\psi_E = RY$ is normalized, we know this:

$$\begin{aligned} 1 &= \iiint_{all\ space} |R(r)Y(\Omega)|^2 dV \\ &= \left(\int_0^\infty |R(r)|^2 r^2 dr\right)\left(\int_{all\ angles} |Y(\Omega)|^2 d\Omega\right). \end{aligned} \tag{A.14}$$

where $d\Omega = \sin\phi\, d\phi\, d\theta$. Declaring both integrals in Line A.14 to be unity, we have thus obtained expressions for independent probabilities in the radial and angular coordinates. We have also placed further restrictions on the solutions of R and Y with this declaration.

A.3 Spherical Harmonics

An additional consequence of the potential's spherical symmetry is that there is no torque acting on the reduced-mass particle, so the angular momentum of the system must be constant. That means ψ_E is an eigenfunction of the angular momentum operator $\hat{L}$. Of course, that means ψ_E is also an eigenfunction of $\hat{L}^2$. Furthermore, since $\hat{L}$ and $\hat{L}^2$ only affect functions of angular coordinates, it is really the function Y within ψ_E that is the eigenfunction; the radial function R is unaffected by the operators.

If we call the eigenvalue of the squared angular momentum operator γ, then

$$\hat{L}^2\, Y_\gamma(\theta,\phi) = \gamma\, Y_\gamma(\theta,\phi). \tag{A.15}$$

Solutions to this equation are called spherical harmonics. Given Equation A.11, we can solve for Y_γ using another round of separation of variables. By the way, since the energy E does not appear in this equation, Y_γ does not depend on E. Letting $Y_\gamma(\theta,\phi) = \Theta(\theta)\,\Phi(\phi)$, Equation A.15 becomes

$$-\hbar^2\left(\Theta''(\theta)\,\Phi(\phi) + \frac{\cos\theta}{\sin\theta}\,\Theta'(\theta)\,\Phi(\phi) + \frac{1}{\sin^2\theta}\,\Theta(\theta)\,\Phi''(\phi)\right) = \gamma\,\Theta(\theta)\,\Phi(\phi), \tag{A.16}$$

or, rearranged,

$$\sin^2\theta\,\frac{\Theta''(\theta)}{\Theta(\theta)} + \sin\theta\cos\theta\,\frac{\Theta'(\theta)}{\Theta(\theta)} + \frac{\gamma}{\hbar^2} = -\frac{\Phi''(\phi)}{\Phi(\phi)}. \tag{A.17}$$

As both sides are independent, each side must equal a constant; we call that constant m^2. (Negative values do not yield physical solutions.) Thus, we have two equations. The azimuthal differential equation implies $\Phi_m(\phi) = e^{im\phi}$, where m must be an integer, positive or negative, to ensure that Φ_m is periodic of period 2π. If we try a negative constant instead of m^2, then the solution for Φ is not cyclic, as it needs to be. These solutions Φ_m result in the relation

$$\hat{L}_z\, Y_{\gamma m}(\Omega) = m\hbar\, Y_{\gamma m}(\Omega). \tag{A.18}$$

The remaining polar differential equation involves both γ and m. After several tricky steps, which we will unfortunately not cover here, one finds that the solutions for $\Theta_{\gamma m}$ are the Legendre polynomials and associated Legendre polynomials with the complication that the

Legendre polynomials P_l ($P_l^m, m = 0$)	Associated Legendre polynomials P_l^m
$P_l(x) = \frac{1}{2^l l!}\frac{d^l}{dx^l}(x^2-1)^l$	$P_l^m(x) = (1-x^2)^{\lvert m\rvert/2}\frac{d^{\lvert m\rvert}}{dx^{\lvert m\rvert}}P_l(x)$
$P_0(\cos\theta) = 1$	
$P_1(\cos\theta) = \cos\theta$	$P_1^1(\cos\theta) = \sin\theta$
$P_2(\cos\theta) = (3\cos^2\theta - 1)/2$	$P_2^1(\cos\theta) = 3\cos\theta\sin\theta$ $P_2^2(\cos\theta) = 3\sin^2\theta$
$P_3(\cos\theta) = (5\cos^3\theta - 3\cos\theta)/2$	$P_3^1(\cos\theta) = 3\sin\theta(5\cos^3\theta - 1)/2$ $P_3^2(\cos\theta) = 15\sin^2\theta\cos\theta$ $P_3^3(\cos\theta) = 15\sin^3\theta$

Table 4: Legendre and associated Legendre polynomials: These functions are the solutions for $\Theta(\theta)$ and happen to be orthogonal.

$Y_{lm}(\theta,\phi) = N_{lm}\,P_l^m(\cos\theta)\,e^{im\phi}$	$N_{lm} = (-1)^m\sqrt{\left(\frac{2l+1}{4\pi}\right)\frac{(l-\lvert m\rvert)!}{(l+\lvert m\rvert)!}}$
Y_{lm} $(m = 0)$	Y_{lm} $(m \neq 0, \lvert m\rvert \leq l)$
$Y_{0,0}(\theta,\phi) = \frac{1}{\sqrt{4\pi}}$	
$Y_{1,0}(\theta,\phi) = \sqrt{\frac{3}{4\pi}}\cos\theta$	$Y_{1,\pm1}(\theta,\phi) = \mp\sqrt{\frac{3}{8\pi}}\sin\theta\,e^{\pm i\phi}$
$Y_{2,0}(\theta,\phi) = \sqrt{\frac{5}{16\pi}}(3\cos^2\theta - 1)$	$Y_{2,\pm1}(\theta,\phi) = \mp\sqrt{\frac{15}{8\pi}}\cos\theta\sin\theta\,e^{\pm i\phi}$ $Y_{2,\pm2}(\theta,\phi) = \sqrt{\frac{15}{32\pi}}\sin^2\theta\,e^{\pm 2i\phi}$
$Y_{3,0}(\theta,\phi) = \sqrt{\frac{7}{16\pi}}(3\cos\theta - 5\cos^3\theta)$	$Y_{3,\pm1}(\theta,\phi) = \mp\sqrt{\frac{21}{64\pi}}(1 - 5\cos^2\theta)\sin\theta\,e^{\pm i\phi}$ $Y_{3,\pm2}(\theta,\phi) = \sqrt{\frac{105}{32\pi}}\cos\theta\sin^2\theta\,e^{\pm 2i\phi}$ $Y_{3,\pm3}(\theta,\phi) = \mp\sqrt{\frac{35}{64\pi}}\sin^3\theta\,e^{\pm 3i\phi}$

Table 5: Normalized spherical harmonics: $Y_{lm}(\theta,\phi) = \Theta_{lm}(\theta)\Phi_m(\phi)$

polynomials take $\cos\theta$ as their arguments rather than θ. These polynomials are shown in Table 4. Given a polynomial solution of degree $k \geq 0$, the eigenvalue becomes $\gamma = (k + \lvert m\rvert)(k + \lvert m\rvert + 1)\hbar^2$. If we define $l \equiv k + \lvert m\rvert$, then we find

$$\gamma = l(l+1)\hbar^2, \tag{A.19}$$

where the degree of the polynomial solution is $l - \lvert m\rvert$, $l \geq 0$, and $\lvert m\rvert \leq l$. The number l, which takes on integer values, is known as the *azimuthal* or *orbital* or *angular quantum number*, and m is known as the *magnetic quantum number*. From here on forward, instead of using the subscripts γ and m, we will use l and m. See Table 5 for the normalized spherical harmonics.

A.4 Laguerre Polynomials

Now we may solve for the radial wave function R. Rewriting Equation A.7, we have that

$$\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2}-\frac{\hbar^2}{\mu r}\frac{\partial}{\partial r}+\frac{\hat{L}^2}{2\mu r^2}-\kappa\frac{e^2}{r}\right]R(r)Y_{lm}(\Omega)=E\,R(r)Y_{lm}(\Omega), \tag{A.20}$$

and using the eigen-nature of Y, this means

$$Y_{lm}(\Omega)\left[-\frac{\hbar^2}{2\mu}\frac{\partial^2}{\partial r^2}-\frac{\hbar^2}{\mu r}\frac{\partial}{\partial r}+\frac{l(l+1)\hbar^2}{2\mu r^2}-\kappa\frac{e^2}{r}\right]R(r)=E\,R(r)Y_{lm}(\Omega). \tag{A.21}$$

If we divide by $Y_{lm}(\Omega)$, then we'll have the differential equation for R alone, and we can easily see that the solutions for R are dependent upon the values of both E and l. So, let these quantities appear as subscripts on R. Then, after dividing by $Y_{lm}(\Omega)$ (no need for the partials anymore) and multiplying by r, we get

$$\left[-\frac{\hbar^2}{2\mu}\left(r\frac{\partial^2}{\partial r^2}+2\frac{\partial}{\partial r}\right)+r\left(\frac{l(l+1)\hbar^2}{2\mu r^2}-\kappa\frac{e^2}{r}\right)\right]R_{El}(r)=rE\,R_{El}(r), \tag{A.22}$$

which is the same as

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2}+\left(\frac{l(l+1)\hbar^2}{2\mu r^2}-\kappa\frac{e^2}{r}\right)\right]rR_{El}(r)=E\,rR_{El}(r). \tag{A.23}$$

Then, if we make the substitution $U_{El}(r)\equiv rR_{El}(r)$, we simply have

$$\left[-\frac{\hbar^2}{2\mu}\frac{d^2}{dr^2}+\frac{l(l+1)\hbar^2}{2\mu r^2}-\kappa\frac{e^2}{r}\right]U_{El}(r)=E\,U_{El}(r). \tag{A.24}$$

Before we move on to solve for U_{El}, though, let's see how it fits into the scheme of things. We declared in Line A.14 the expression for finding the radial-dependent probabilities of the wavefunction. Now we can see that it is natural to look at the function $U_{El}(r)=rR_{El}(r)$ because its magnitude squared is the radial probability density:

$$1=\int_0^\infty |R_{El}(r)|^2 r^2 dr=\int_0^\infty |U_{El}(r)|^2 dr. \tag{A.25}$$

Okay, now let's solve for $U_{El}(r)$. It appears that we are solving a one-dimensional particle-in-a-potential problem, where the domain is from zero to infinity and the potential (in Equation A.24) has an attractive Coulomb part and a repulsive centrifugal part that depends on the angular momentum. We will have to do some investigation to find the boundary constraints on $U_{El}(r)$. Let's call the operator in Equation A.24 $\hat{D}$ so that $\hat{D}U_{El}=EU_{El}$. We want to find solutions such that $\hat{D}$ is Hermitian with respect to them. So if we have two solutions U_a and U_b, then $\langle U_a|\hat{D}U_b\rangle=\langle U_a|\hat{D}|U_b\rangle=\langle U_b|\hat{D}^\dagger|U_a\rangle^*=\langle U_b|\hat{D}|U_a\rangle^*=\langle U_b|\hat{D}U_a\rangle^*=\langle \hat{D}U_a|U_b\rangle$, or

$$\int_0^\infty {U_a}^*(\hat{D}U_b)\,dr=\int_0^\infty (\hat{D}U_a)^*U_b\,dr. \tag{A.26}$$

Plugging in the explicit form of $\hat{D}$ and simplifying, we get

$$\int_0^\infty {U_a}^* \left(\frac{d^2}{dr^2} U_b\right) dr = \int_0^\infty \left(\frac{d^2}{dr^2} U_a\right)^* U_b \, dr, \tag{A.27}$$

or

$$\int_0^\infty {U_a}^* \, d\!\left(\frac{d}{dr} U_b\right) = \int_0^\infty U_b \, d\!\left(\frac{d}{dr} {U_a}^*\right). \tag{A.28}$$

Using integration by parts (and the notation $U' = dU/dr$), this is the same as

$$\left[{U_a}^* \, {U_b}'\right]_0^\infty - \int_0^\infty {U_a}^{*\prime} \, {U_b}' \, dr = \left[U_b \, {U_a}^{*\prime}\right]_0^\infty - \int_0^\infty {U_b}' \, {U_a}^{*\prime} \, dr, \tag{A.29}$$

or, more simply,

$$\left[{U_a}^* \, {U_b}' - U_b \, {U_a}^{*\prime}\right]_0^\infty = 0. \tag{A.30}$$

Since any solution U_{El} must be square-integrable (see Equation A.25), U_{El} must go to zero as r goes to infinity, so the expression in brackets in Equation A.30, evaluated at infinity, is zero. Thus the expression must also be zero at $r = 0$.

If any solution U_{El} approaches a constant $c \neq 0$ as r approaches zero, then

$$\psi(\mathbf{r}) = R_{El}(r) \, Y_{lm}(\theta, \phi) = \frac{U_{El}(r)}{r} \, Y_{lm}(\theta, \phi) \sim \frac{c}{r} \, Y_{lm}(\theta, \phi) \tag{A.31}$$

near $r = 0$. However, this does not satisfy the time-independent Schrödinger equation (Equation A.20) because the Laplacian (which is broken into two terms in Equation A.20) generates a Dirac delta: $\nabla^2(1/r) = -4\pi\delta(\mathbf{r})$. So U_{El} must approach zero as r goes to zero. That result also takes care of the relation in Equation A.30.

Looking again at the differential equation that describes U_{El} (Equation A.24), we can find out more about the character of the solutions by examining the equation near the boundaries. Here's the equation again, rearranged:

$${U_{El}}''(r) = \left[-\frac{2\mu E}{\hbar^2} + \frac{l(l+1)}{r^2} - \frac{2\mu\kappa e^2}{r}\right] U_{El}(r). \tag{A.32}$$

As r approaches zero, the centrifugal term will dominate, thus, near zero,

$${U_{El}}''(r) \simeq \frac{l(l+1)}{r^2} \, U_{El}(r). \tag{A.33}$$

This suggests that, near zero, U_{El} is similar to r^α, where $\alpha(\alpha-1) = l(l+1)$; that is, $\alpha = (l+1)$ or $(-l)$. Since one of our boundary conditions is that U_{El} be equal to zero at $r = 0$, we can only accept $\alpha = (l+1)$, so

$$U_{El}(r) \sim r^{l+1} \tag{A.34}$$

near zero. As r goes to infinity, we have

$${U_{El}}''(r) \simeq -\frac{2\mu E}{\hbar^2} \, U_{El}(r). \tag{A.35}$$

For bound states, where $E < 0$, we conclude that

$$U_{El}(r) \sim \exp\left[-\sqrt{-2\mu E/\hbar^2}\, r\right] \tag{A.36}$$

for large r. We'll let $\lambda = \sqrt{-2\mu E/\hbar^2}$ to simplify that expression. So now we know what U_{El} looks like as it approaches its boundaries, but what goes on in between?

We shall make an assumption about U_{El}: that it can be expressed as a the product of the two boundary functions, r^{l+1} and $e^{-\lambda r}$, and some polynomial or power series in r. Let that polynomial be called $p(r)$ and let

$$p(r) = \sum_{j=0}^{\infty} a_j r^j. \tag{A.37}$$

If we plug our proposed solution $U_{El}(r) = r^{l+1}e^{-\lambda r}p(r)$ back into the differential equation describing U_{El} (Equation A.24) and simplify, then we have

$$p'' + 2\left(\frac{l+1}{r} - \lambda\right)p' + 2\left(\frac{\mu\kappa e^2/\hbar^2 - \lambda(l+1)}{r}\right)p = 0, \tag{A.38}$$

where we now see that the solutions for p depend on E (through λ) and l. So we have p_{El}. Since ${p_{El}}'(r) = \sum_{j=0}^{\infty}(j+1)a_{j+1}r^j$ and ${p_{El}}''(r) = \sum_{j=0}^{\infty}(j+2)(j+1)a_{j+2}r^j$, Equation A.38 gives us

$$\sum_{j=0}^{\infty}\Big[(j+2)(j+1)a_{j+2}r^j + 2(l+1)(j+1)a_{j+1}r^{j-1}$$
$$-2\lambda(j+1)a_{j+1}r^j + 2\left(\mu\kappa e^2/\hbar^2 - \lambda(l+1)\right)a_j r^{j-1}\Big] = 0. \tag{A.39}$$

Note that in this sum there are only two terms with r^{-1}, but there are four terms with each successive power of r. If we collect all terms with the same power of r, then each resulting coefficient must be equal to zero for the entire sum to be zero. That leads to the fact that we can use an equation for each coefficient to obtain relationships between the a_n's. For the first coefficient, the equation looks like this: $2(l+1)(j+1)a_j = 2[\lambda(l+1) - \kappa e^2\mu/\hbar^2]a_{j-1}$ for $j = 0$. For all other coefficients ($j \geq 1$), we obtain a recurrence relation that looks like this:

$$j(j + 2\lambda + 1)a_j = 2[\lambda(j+l) - \mu\kappa e^2/\hbar^2]a_{j-1}. \tag{A.40}$$

It just so happens that this agrees with the first equation, so this relation is true for all $j \geq 0$.

So what does this recurrence relation tell us? Well, if we want to check to see if our proposed $U_{El}(r)$ behaves like it should at the boundaries, now we can. The boundary of r approaching zero is fine since $p_{El}(r)$ will only approach a constant a_0, allowing U_{El} to approach zero as it should. We still have to check the behavior of the polynomial when r is large, though. As r approaches infinity (or whenever r is larger than 1) the coefficients of the larger powers of r have the most influence on the behavior of $p_{El}(r)$. Let's see what the recurrence relation for the coefficients looks like for large powers of r:

$$\lim_{j\to\infty} a_j = \lim_{j\to\infty}\left(\frac{2[\lambda(j+l)-\mu\kappa e^2/\hbar^2]}{j(j+2\lambda+1)}a_{j-1}\right) = \frac{2\lambda}{j}a_{j-1}. \tag{A.41}$$

So, the larger the power of r, the more the coefficients obey this recurrence relation. This relation, though, is the same as the recurrence relation for the coefficients of $e^{2\lambda r}$. So for large r, if we assume that $p_{El}(r)$ is an infinite polynomial then it behaves like $e^{2\lambda r}$, and

$$U_{El}(r) \sim r^{l+1}e^{-\lambda r}e^{2\lambda r} \sim e^{\lambda r}. \tag{A.42}$$

But this contradicts the requirement that $U_{El}(r)$ behave as $e^{-\lambda r}$ for large r. That means p_{El} cannot be an infinite polynomial; it must terminate at some point. In this case, $p_{El}(r)$ will not affect our requirement that $U_{El}(r)$ be dominated by $e^{-\lambda r}$ for large r.

Assuming $p_{El}(r)$ is a finite polynomial, there must be some coefficient a_{N+1} that equals zero, where $N \geq 0$. The recurrence relation (Equation A.40) will guarantee that all following coefficients will be zero as well. The relation also implies that

$$\lambda(N+1+l) - \mu\kappa e^2/\hbar^2 = 0. \tag{A.43}$$

If we define $n \equiv N+l+1$ and recall that $\lambda = \sqrt{-2\mu E/\hbar^2}$, then this is equivalent to the relation

$$E = -\frac{\mu\kappa^2 e^4}{2\hbar^2}\frac{1}{n^2}. \tag{A.44}$$

This looks familiar, doesn't it? Since n is now synonymous with E, we shall substitute n for the subscript E. Here, n is called the *principal quantum number* and N is called the *radial quantum number*. By the relations and definitions presented so far, we have that $0 \leq l \leq n-1$, and $n \geq 1$. So, given a particular value of n, there are n values for l to take. Remember also that for a given value of l, there are $2l+1$ values for m to take since $|m| \leq l$. In total, then, for each energy state with its particular value of n, there are n^2 combinations of the quantum numbers l and m.

Let's get back to the matter of the coefficients of p_{nl}. We have determined that p_{nl} is a finite polynomial of degree $N = n-1-l$, and we know a recurrence relation that can produce all coefficients given any one coefficient. We also have the condition that the function $U_{nl}(r) = r^{l+1}e^{-\lambda r}p_{nl}(r)$, when squared and integrated over the domain of r, yields unity. Since squaring $U_{nl}(r)$ will only lead to more polynomials multiplied by exponentials, and since we know $\int_0^\infty r^n e^{ar} = n!/a^{n+1}$, we can conclude that it is possible to find all coefficients such that U_{nl} is normalized. The unnormalized solutions for p_{nl}, which are called the Laguerre polynomials and associated Laguerre polynomials, are shown in Table 6.

It is convenient to use a constant a_0 called Bohr's radius, where $a_0 = \hbar^2/\mu\kappa e^2$, in the radial solutions. With this constant, $\lambda = 1/na_0$ and

$$E = -\frac{\kappa e^2}{2a_0}\frac{1}{n^2}. \tag{A.45}$$

Table 7 presents the normalized radial solutions in terms of Bohr's constant.

Laguerre polynomials L_i ($L_i^j, j = 0$)	Associated Laguerre polynomials L_i^j
$L_i(r) = e^r \frac{d^i}{dr^i}(r^i e^{-r})$	$L_i^j(r) = \frac{d^j}{dr^j} L_i(r)$
$L_0(r) = 1$	
$L_1(r) = 1 - r$	$L_1^1(r) = -1$
$L_2(r) = 2 - 4r + r^2$	$L_2^1(r) = -4 + 2r$ $L_2^2(r) = 2$
$L_3(r) = 6 - 18r + 9r^2 - r^3$	$L_3^1(r) = -18 + 18r - 3r^2$ $L_3^2(r) = 18 - 6r$ $L_3^3(r) = -6$

Table 6: Laguerre and associated Laguerre polynomials: These functions are the solutions for $p_{nl}(r)$ and happen to be orthogonal.

$R_{nl}(r) = N_{nl} \left(\frac{2r}{na_0}\right)^l e^{-r/na_0} L_{n+l}^{2l+1}\left(\frac{2r}{na_0}\right)$	$N_{nl} = -\left[\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}\right]^{1/2}$
R_{nl} $(l = 0)$	R_{nl} $(1 \leq l \leq n-1)$
$R_{1,0}(r) = \frac{1}{2\sqrt{a_0^3}} e^{-r/a_0}$	
$R_{2,0}(r) = \frac{1}{\sqrt{2a_0^3}} \left(1 - \frac{r}{2a_0}\right) e^{-r/2a_0}$	$R_{2,1}(r) = \frac{1}{\sqrt{6a_0^3}} \left(\frac{r}{2a_0}\right) e^{-r/2a_0}$
$R_{3,0}(r) = \frac{2}{3\sqrt{3a_0^3}} \left(1 - \frac{2r}{3a_0} + \frac{2r^2}{27a_0^2}\right) e^{-r/3a_0}$	$R_{3,1}(r) = \frac{8}{9\sqrt{6a_0^3}} \left(1 - \frac{r}{6a_0}\right) \left(\frac{r}{3a_0}\right) e^{-r/3a_0}$ $R_{3,2}(r) = \frac{4}{9\sqrt{30a_0^3}} \left(\frac{r}{3a_0}\right)^2 e^{-r/3a_0}$

Table 7: Normalized radial solutions: $R_{nl}(r) = r^l e^{-\lambda r} p_{nl}(r)$.

So, finally we have the solutions for the bound states of the hydrogen atom. $\Psi(\mathbf{R},\mathbf{r},t) = \chi(\mathbf{R})\,\psi(\mathbf{r})\,\tau(t)$, where χ and τ were given earlier in Equations A.9 and A.10, respectively, and

$$\begin{aligned}
\psi(\mathbf{r}) &= R_{nl}(r)\,Y_{lm}(\Omega) && \text{(A.46)}\\
&= \frac{1}{r}\,U_{nl}(r)\,\Theta_{lm}(\theta)\,\Phi_m(\phi) && \text{(A.47)}\\
&= N_{nl}\left(\frac{2r}{na_0}\right)^{l} e^{-r/na_0}\,L_{n+l}^{2l+1}\!\left(\frac{2r}{na_0}\right)\,N_{lm}\,P_l^m(\cos\theta)\,e^{im\phi}, && \text{(A.48)}
\end{aligned}$$

where

$$N_{nl} = -\left[\left(\frac{2}{na_0}\right)^3 \frac{(n-l-1)!}{2n[(n+l)!]^3}\right]^{1/2} \tag{A.49}$$

and

$$N_{lm} = (-1)^m\sqrt{\left(\frac{2l+1}{4\pi}\right)\frac{(l-|m|)!}{(l+|m|)!}} \tag{A.50}$$

B Spline Equations

In section 2.2.4, we presented fifth degree splines and the boundary conditions that the splines fulfill, and we even graphed examples of them. However, the formulae for the quintic splines were not shown in that section. They are shown below:

$$S_{\iota 00}(r) = -\frac{(r-r_{\iota-1})^3(6r^2+{r_{\iota-1}}^2+r_{\iota-1}(3r-5r_\iota)-15rr_\iota+10{r_\iota}^2)}{(r_{\iota-1}-r_\iota)^5} \tag{B.1}$$

$$S_{\iota 01}(r) = \frac{(r-r_{\iota+1})^3(6r^2+10{r_\iota}^2+3rr_{\iota+1}+{r_{\iota+1}}^2-5r_\iota(3r+r_{\iota+1}))}{(r_\iota-r_{\iota+1})^5} \tag{B.2}$$

$$S_{\iota 10}(r) = -\frac{(r-r_{\iota-1})^3(3r+r_{\iota-1}-4r_\iota)(r-r_\iota)}{(r_{\iota-1}-r_\iota)^4} \tag{B.3}$$

$$S_{\iota 11}(r) = -\frac{(r-r_\iota)(r-r_{\iota+1})^3(3r-4r_\iota+r_{\iota+1})}{(r_\iota-r_{\iota+1})^4} \tag{B.4}$$

$$S_{\iota 20}(r) = -\frac{(r-r_{\iota-1})^3(r-r_\iota)^2}{2(r_{\iota-1}-r_\iota)^3} \tag{B.5}$$

$$S_{\iota 21}(r) = \frac{(r-r_\iota)^2(r-r_{\iota+1})^3}{2(r_\iota-r_{\iota+1})^3} \tag{B.6}$$

C Antimatter Theory

This appendix is a short note to those who are unfamiliar with antimatter. Basically, each elementary particle has a corresponding “antiparticle,” a particle which is essentially exactly like the original particle except that it has opposite charge. The antiparticle version of the electron is called the positron, and it has the same mass as the electron and same magnitude of charge, but it is positively charged. Antiprotons have negative charge and are made out of the antiquarks that correspond to the quarks in a proton. This change in sign of charge from particle to antiparticle is all that is important to the particular problem presented in this paper. We could just as easily be talking about the hydrogen atom rather than the antihydrogen atom, but we refer to the antimatter version to keep in mind the experimental application with which we are interested. Much more could be said about antimatter, such as annihilation of particles with antiparticles, and about particle physics in general, but it is unnecessary for the problem at hand.