

# Solving the Helium Atom

Or: Why does Chemistry Exist?

Matthew Reed

Math 164 – Scientific Computing

May 4, 2007

## 1. Motivation

One of the first real-world calculations demonstrated in any introductory quantum mechanics class is the hydrogen atom. It is surprisingly straightforward to find the ground state (lowest energy) solution for any so-called “hydrogenic” atom. Hydrogenic atoms are nuclei of any charge with exactly one bound electron. Indeed, with slightly more advanced methods easily accessible to undergraduates, the entire excitation spectrum of a hydrogenic atom can be calculated. Any atomic system more complicated than this is, however, analytically intractable. We shall seek to find the ground state energy of the helium atom as a test system for the so-called Hartree-Fock approximation. This method can, in principle, be used to calculate very complicated quantum systems like molecules with good accuracy and speed.

## 2. Background

Before we get started, however, we will briefly review the principles of quantum mechanics. Particles do not actually have specific positions or many other qualities we attribute to macroscopic objects. Rather, they are described by “wave functions” which determine the *probability* of a particle being found in a certain area, traveling with a certain momentum, and so on. Certain quantities can be precisely set for particles that are in “eigenstates” of that observable, and the same eigenstates can correspond to multiple observables (which are then said to “commute” with one another.) Electrons orbiting hydrogen, for example, have an exactly determined energy, total angular momentum, and angular momentum component along the z-axis. Particles can also be in *superpositions* of multiple eigenfunctions, meaning that they have certain probabilities of being found in particular eigenstates. Such states are fundamentally

undetermined (the particle is *actually* in several places, or traveling at several speeds), until a measurement is made which forces it to “choose one.” Wave functions contain all information that it is possible to know about a particle; there are no “hidden variables” that tell how the particle will choose to be measured when in a superposition – it is fundamentally random. Therefore, if one can determine the wavefunction of a particle (known as “solving” for the particle), one knows everything physics can predict.

Wavefunctions are calculated by solving the Schrödinger equation, given below in one of its many forms:

$$\hat{H}(t)|\psi\rangle = i\hbar \frac{\partial}{\partial t}|\psi\rangle$$

where  $i$  is  $\sqrt{-1}$ ,  $\hbar$  is a physical constant setting the energy scale of quantum effects, and  $|\psi\rangle$  is the wavefunction.  $\hat{H}(t)$  is known as the “Hamiltonian,” and is an “operator” which acts on a wavefunction to get its energy. It can take virtually any form, but for the special case of a massive particle being acted on by an external potential  $V$ , it looks like:

$$\hat{H} = -\frac{\hbar^2}{2m}\nabla^2 + V(\vec{r}, t).$$

$V$  can again be virtually anything. In the simplest case of a central Coulomb potential of charge  $Z$ , as we would have for the hydrogen atom,  $V$  is taken to be:

$$V(\vec{r}) = -\frac{Ze^2}{|\vec{r}|}.$$

As with all differential equations, there are precious few forms  $V$  can take which are analytically solvable. As mentioned before, hydrogen is one of them, but, sadly, helium (or indeed any other atom) is not.

The difficulty with solving helium comes from the fact that there are electron-electron interactions. With only one electron, the entire proton-electron interaction can be packaged into the electron (e.g. the proton is unaffected by the electron) by using something called the “reduced mass” instead of the actual electron mass. Unfortunately, no such algebraic trick exists with more than two bodies. Each electron affects the other, meaning that the potential is a function of the wavefunction itself. This makes the Schrödinger equation quite complicated. Even with the best mathematical tricks, calculating the ground state energy of the second electron of helium constitutes an infinite sum of highly non-trivial integrals. (As an aside, it does

not actually make sense to say the “second” electron. Electrons are fundamentally indistinguishable particles – you cannot tell one from the other – so the *single* electronic wavefunction of helium actually describes the probability of *two* electrons.) Fortunately, there are some reasonable approximations one can make to get a good estimate of the wavefunction and its energy.

### 3. Approximations

One such commonly used method is known as the Hartree-Fock approximation. Rather than treating electrons as indistinguishable particles as they truly are, it assumes that each is described by its own independent wave function. Calculations can then be made on one while holding the other constant, vastly simplifying the equations to be solved. This process is iterated until the solution converges to some threshold. All solutions must be found numerically, but they are well suited to standard computational methods. The Hartree-Fock approximation has an extremely large range of applicability; it is not just for helium. Calculating the wave functions for molecules, for example, can be done. Indeed, one of the most common examples of the method is to calculate the binding energy of a  $H_2$  molecule.

There are several other approximations built into the Hamiltonian we choose. We are assuming that the electron is nonrelativistic, which is a good approximation for small atoms. For hydrogen, the characteristic velocity is only about  $1/137$  the speed of light, meaning the  $\gamma$  factor, which sets the size scale of relativistic corrections, is less than 1.00003. (In the nonrelativistic limit,  $\gamma$  is assumed to be 1.) For very large atoms such as uranium, relativistic effects are very important (and even dominate), so this treatment would not be sufficient for them. Helium should be fine though.

We also ignore some other second-order terms in the Hamiltonian. The spin-orbit coupling between the intrinsic magnetic spin of the nucleus and the electrons are ignored, which contribute an energy on the same order as relativity. The “Darwin term” coming from quantum electrodynamics and the interactions of electrons with virtual vacuum positrons is similarly ignored, and would also contribute an energy on the same order as relativistic corrections. Interactions with external magnetic fields and electron-electron spin interactions are also left out. All these terms are a great deal smaller than our expected numerical uncertainty, so including them would be meaningless.

## 4. Mathematical Methods

In the special case of ground-state helium, there is some useful symmetry we can take advantage of. The wave functions of both electrons will be spherically symmetric, and so proportional to a function of only the scalar coordinate  $r$ . This proportionality constant is set by the requirement that the probability of finding the particle anywhere should be exactly one. Thus we have for one electron:

$$\psi(x) = \frac{1}{(4\pi)^{1/2} r} R(r) \left| \pm \frac{1}{2} \right\rangle.$$

The  $\pm 1/2$  factor in the bracket at the end indicates the intrinsic spin of the particle, which may be either positive or negative. When combining the two wave functions into the overall electronic structure, we must be careful about something called exchange symmetry. Because an electron is a “fermion,” exchanging (e.g. flipping labels) identical particles must cause the wave function to change in sign. The physical interpretation of this is that two fermions cannot occupy the same quantum state. (Other types of particles, known as bosons, can occupy the same state, and even prefer to in some obtuse way. Normally this distinction makes little difference at finite temperature, but it is crucial for the understanding of things like the electronic structure of solids.) The overall wavefunction then must take the form:

$$\psi(x) = \frac{1}{\sqrt{2}} \frac{1}{4\pi r_1 r_2} R_1(r) R_2(r) \left[ \left| +\frac{1}{2} \right\rangle_1 \left| -\frac{1}{2} \right\rangle_2 - \left| -\frac{1}{2} \right\rangle_1 \left| +\frac{1}{2} \right\rangle_2 \right]$$

where the notation  $|+\frac{1}{2}\rangle_1 |-\frac{1}{2}\rangle_2$  indicates that the first electron has spin up, while the second has spin down.

The potential seen by one particle then becomes the sum of the attraction to the proton’s charge and the repulsion from the charge distribution of the other electron. We say that the energy of this radial  $R(r)$  state is given by:

$$E = \frac{\hbar^2}{m} \int_0^\infty \left( \frac{dR}{dr} \right)^2 dr + \int_0^\infty \left[ -\frac{Ze^2}{r} + \frac{1}{4} \Phi(r) \right] \rho(r) 4\pi r^2 dr$$

where  $\rho(r) = R^2(r)/2\pi r^2$ . We can find the ground state of the radial wave function through the calculus of variations. The ground state is guaranteed to have the lowest possible energy of any

normalized (e.g. total probability equal to one) wave function. If we consider the expression for energy above to be a functional, we can require that for any arbitrary variation  $\delta R(r)$ :

$$\delta \left( E - 2\varepsilon \int_0^{\infty} R^2 dr \right) = 0$$

Enforcing this requirement leads to, through the methods of variational calculus:

$$\int_0^{\infty} \delta R(r) \left[ -4 \frac{\hbar^2}{2m} \frac{d^2}{dr^2} - 4 \frac{Ze^2}{r} + 2\Phi(r) - 4\varepsilon \right] R(r) dr = 0$$

This requirement is satisfied when  $R(r)$  satisfies the following eigenvalue equation:

$$\left[ -\frac{\hbar^2}{2m} \frac{d^2}{dr^2} - \frac{Ze^2}{r} + \frac{1}{2}\Phi(r) - \varepsilon \right] R(r) = 0. \quad (1)$$

The eigenvalue  $\varepsilon$  is a Lagrange multiplier ensuring that the function is normalizable. It also has the useful physical interpretation of being the single-particle ionization energy.

In addition to equation (1), we need an expression that relates  $R(r)$  to the potential  $\Phi$  it creates for the other electron. This additional equation is simply Poisson's equation, given by

$$\frac{1}{r^2} \frac{d}{dr} \left( r^2 \frac{d\Phi}{dr} \right) = -4\pi e^2 \rho.$$

In order to avoid the singularity at the origin with this equation, we use the change of variables  $\Phi(r) = r^{-1}\phi(r)$ , which simplifies Poisson's equation to

$$\frac{d^2\phi}{dr^2} = -4\pi e^2 r \rho. \quad (2)$$

Thus we have mathematical basis for both steps of the Hartree-Fock approximation: finding the radial wavefunction and then calculating the resulting potential.

## 5. Numerical Methods

The first means we attempted to use to solve these equations was the shooting method. Coded in Mathematica, we were able to make a complete program to do the process in principle. However, this method turned out to be inappropriate for this application. Finding the eigenvalue, for example, is extremely sensitive. If it is off by even the limits of machine precision, at finite length the radial wave function will explode exponentially. And unfortunately, the eigenvalue

will always be slightly off, be it by limitations of the search algorithm or by numerical error; thus, the solution will always explode at a large enough radius (often only 5 to 10 angstroms). This is fundamentally a reflection of the underlying physics: there truly are only discrete energy levels allowed to the particle, and even a tiny deviation from this allowed value is unphysical. While Mathematica is well suited for many problems, this turned out to not be one of them.

We instead looked to a finite differences method using Mathematica. By discretizing the space and approximating derivatives as finite differences between discrete values, we can turn the problem from a continuous differential equation into a matrix eigenvalue problem. The eigenvalues of the matrix in question are then the energies of the associated eigenvectors, which are lists of the values the radial wavefunction takes. This method has the distinct advantage of being exact; the radial wavefunction is guaranteed to not exponentially explode at large radius.

Originally, a second order accurate scheme was used. These equations are well known and available, but have somewhat limited accuracy compared to alternatives. After seeing that the equations did not converge as quickly as was hoped, however, a fourth-order scheme was implemented. This required the derivation of non-centered equations. This can be done by “fitting” an  $N^{\text{th}}$  order polynomial to  $N$  data points, differentiating the resulting polynomial as necessary, and evaluating it at a given point. By this method we derived several equations, including the following, which is a left-centered 4<sup>th</sup> order 2<sup>nd</sup> derivative:

$$y''(0) \approx \frac{35y(0) - 104y(1) + 114y(2) - 56y(3) + 11y(4)}{12\Delta x^2}.$$

The size and boundary conditions of the matrix were varied in order to explore the convergence behavior. In principle, as the dimension of the matrix and the boundary condition goes to infinity, the energy and wavefunction should approach their exact values. Unfortunately, there is no particular guarantee that this convergence should happen quickly. In particular, solving to a larger radius dramatically increases computational time. Understanding the reason for this requires some further explanation of the particular computational methods used.

The method of finding eigenvalues in the sparse matrix we create, MATLAB’s built-in `eigs` function, can return the  $N$  smallest eigenvalues in magnitude relatively quickly. This is good, since the ground state energy we are interested in is by definition the smallest (most negative) value. Especially for large matrices, a lot of the eigenvectors tend to correspond to completely unphysical unbound states with very large positive energies. Unfortunately, it is not

ideal – it returns only the smallest eigenvalues in *magnitude*, rather than in value. That means that all the excited bound states, with less negative energies, but smaller absolute magnitudes, are found by `eigs` before the solution we are interested in. (There are also unphysical unbound states with relatively small positive energies that come before ours.) The number of the bound state solutions that can be found is directly proportional to the radius we solve out to (since there is more space to distinguish them), so we have to find more and more eigenvalues before the relevant one for larger systems. Finding an eigenvalue, even in a sparse matrix, is a computationally expensive procedure, and this process takes by far the longest of any involved in the calculation.

Fortunately, only solving for the radial wave function requires this care. Calculating the potential is a comparatively easy task, requiring only the solution to a linear system of equations, since no eigenvalue needs to be decided on. A matrix describing the discretized differential equation is still used, but a vector of boundary conditions multiplies its inverse to get the unique solution. MATLAB can do this operation very quickly, especially with sparse matrices, through the use of its “/” operator.

## 6. Results

We chose the largest value of  $N$  and radial extent possible. This was limited by both the memory available on our computer (1.5 gigabytes) and by time constraints. The longest calculation we did, with  $N=200,000$  and  $L=150$ , took approximately eight hours to complete on a dual processor 2GHz G5 computer. Unfortunately, even with these considerable computational resources, the calculated energies disagreed with reality by a reasonably large amount.

In virtually all reasonable (e.g.  $L$  greater than 5) cases, the value for the first ionized state was calculated to be the same value independent of parameters: **-54.46eV**. This compares to a true value of  $-54.42\text{eV}$ , a difference of 0.07%. That is reasonably impressive, though entirely useless from a practical standpoint. A one-electron atomic system, as mentioned before, can be calculated analytically. A plot of the wavefunction we found is shown below, in figure 1.

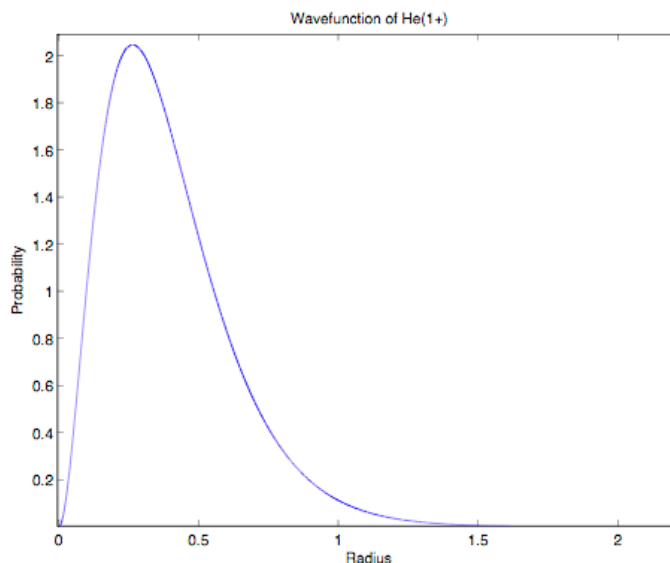


Figure 1. Wavefunction of the first ionized state of helium. The axes here are radius in angstroms from the proton on the x-axis and probability on the y-axis. For example, it is most likely to find the electron at approximately  $R=0.4\text{\AA}$ .

The value for the interesting energy, the ground state of neutral helium, turned out to be more sensitive to the numerical parameters, but very slow to converge. For the most intensive calculation,  $N=200,000$  and  $L=150$ , we calculated an energy of the second bound electron of  $-25.21\text{eV}$ , compared to an experimental value of  $-25.59\text{eV}$ . This is a difference of about 1.5%, dramatically more error than previously encountered. Less complicated calculations do not appear to make a significant difference;  $N=200,000$  and  $L=50$  yields a value of  $-25.25\text{eV}$ . A plot of the corresponding wavefunction is shown below, in figure 2.

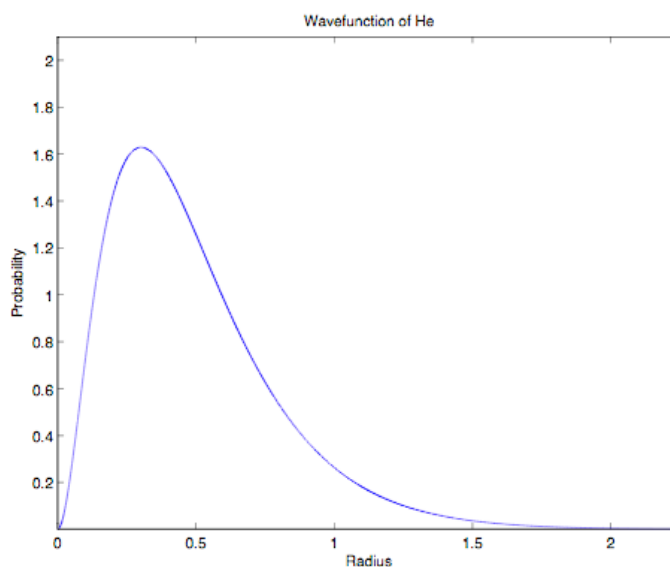


Figure 2. Wavefunction of the first ionized state of helium. Note that this electron's wavefunction is more spread out, corresponding to a lower energy than  $\text{He}^*$ .



## 7. Discussion

The fact that, independent of the numerical parameters of the problem, our value for the ground state of ionized helium is off by a constant is interesting. It means that there is either some inherent offset in our numerical method that remains (perhaps a bug), or that the physical constants being fed into the computer are slightly off. Either way, this is an error that is likely responsible for a reasonably large amount of our error. Every time we iterate the Hartree-Fock algorithm, this error is compounded, throwing the solution trajectory further and further from the true value. Indeed, if the problem is in one of the physical constants, the error would be compounded both when calculating the wavefunction and the potential.

The value for the ground state of neutral helium does, however, get better with more intense computation. Thus, some of our uncertainty comes from numerical error. It does not appear that increasing the size of the matrix  $N$  significantly affects precision, especially since we are using a 4<sup>th</sup> order accurate scheme. Unfortunately, as described above, the rate of convergence with respect to the length parameter is very slow. Compounding this issue is the fact that the calculation time is a strong function of this parameter. This issue could be dramatically ameliorated if some method of finding the eigenvalues that was fast and had no dependence on the length were found. Unfortunately, one does not appear to exist. Alternatively, an entirely new numerical method, distinct from both finite differences and the shooting method, might be considered.

## 7. Conclusions

The Hartree-Fock method is a viable means for calculating complex quantum systems for which no analytic solution exists. As we have seen, however, the success of the calculation is highly dependent on the numerical methods selected. We were unable to calculate helium's energy to a precision greater than 1.5%, even with advanced software and computers. The fact that this method has been used with considerable success for decades indicates that perhaps better numerical methods exist. Perhaps using FORTRAN instead of MATLAB or Mathematica would have bore more fruit, or an entirely different numerical scheme entirely. Nevertheless, we have demonstrated a powerful numerical technique which is surprisingly easy to set up, and which yields results that pose genuine theoretical challenges.

Future work could include trying to track down the offset in the radial wavefunction calculation, and verifying the values used for constants. Other numerical methods could be explored, and possibly different algorithms for finding eigenvalues. The ambition of the calculation could be increased to trans-helium atoms, where radial symmetry is broken, as well. This would require solving of several differential equations simultaneously, for both the radial and angular components of the wavefunctions.