

Energies of the Lithium Atom Using Undergraduate Quantum Mechanics

Megan Tabbutt

Physics Department, University of Wisconsin-Madison.

(Dated: April 29, 2018)

With three electrons the Lithium atom can be used as a simple model of how the energy levels of an atom are affected by and must obey the Pauli Exclusion Principle. Through undergraduate level quantum mechanics [5] and the use of the computer software, Mathematica [4], we were able to calculate the energies of the low lying states of Lithium. We found the ground state to be -7.42115 Hartrees, 0.759904% different from the value found in the Energy Level Database of the National Standards of Science and Technology (NIST) [2]. The method included using a variational analysis and representing the Hamiltonian of Lithium in a basis of Slater Determinates. A quantum defect analysis was also performed and the defect was found to be 0.408504, 1.82407% different than the NIST value [2].

I. INTRODUCTION

The Lithium atom has 3 electrons and as such proves more difficult in the calculation of the wave functions and energy levels than one or two electron atoms. In order to calculate the wave functions and energy levels we will need to be careful in our use of the Pauli Exclusion Principle to ensure that we are adhering to it strictly. Despite this complication, Lithium has the benefit of being the simplest and lightest atom to consider that has this added constraint. We first followed the methodology presented in the Masse & Walker paper [1] to analyze the Li^+ ion. In this paper a method is presented for finding the wave functions and energy levels of the two electron He atom. This analysis differs from ours because with only 2 electrons you are able to utilize product bases and do not need to expand your Hamiltonian in a basis of Slater Determinates. Here we present an analysis of the low lying energy levels of the Lithium atom using Quantum Mechanics accessible to an undergraduate level [5] as well as the use of Mathematica software [4]. Using the variational principle and representing the Hamiltonian in a basis of Slater Determinates we were able to obtain the ground state energy to less than 1% and the Quantum Defect to less than 2%.

It is typical in undergraduate quantum mechanics courses to talk about the wave functions and energy levels of the Hydrogen and Helium atoms as they are simpler than Lithium. Hydrogen doesn't need to take the Pauli Exclusion Principle into account at all and for Helium we can use the rudimentary exclusion principle that the quantum numbers of the two electrons just need to be different. We cannot use this more simple idea of the exclusion principle for the 3 electron Lithium atom.

For this project we want to calculate a few of the low lying energy states in Lithium. The Hamiltonian that we will be using can be written, in scaled unites, as [5]:

$$\hat{H} = \hat{H}_0 + V_{12} + V_{13} + V_{23} \quad (1)$$

V_{ij} , is the coulomb potential interaction between the i th and j th electrons. \hat{H}_0 can be written as: $\hat{H}_0 =$

$\hat{H}_0^{++}(1) + \hat{H}_0^{++}(2) + \hat{H}_0^{++}(3)$, where, $\hat{H}_0^{++}(1)$ is the hamiltonian for a single electron Li^{++} atom that is Hydrogenic, and has a nucleus charge of $Z = 3$. In this way, $\hat{H}_0^{++}(1)$ can be written in the standard manner as [5]:

$$\hat{H}_0^{++}(1) = -\frac{1}{2}\nabla^2 - \frac{Z}{r} \quad (2)$$

This is the form of the Hamiltonian that we used throughout our analysis and which can be seen in Figure 1. It should also be noted that all energies are reported in Hartrees, where $1 \text{ Ha} = 2 \text{ Ry}$, and 1 Rydberg is defined as: $1 \text{ Ry} \equiv hcR_\infty = \frac{m_e e^4}{8\epsilon_0^2 h^2} = 13.605693009 \text{ eV}$ [3].

II. THE PAULI EXCLUSION PRINCIPLE

The Pauli Exclusion Principle states that the wave function of an electron needs to be antisymmetric under exchange, it is not sufficient to state that the quantum numbers merely need to be different for each electron. Each electron having a unique set of quantum numbers is sufficient to satisfy the Pauli Exclusion Principle with just two electrons, but is not for atoms with 3 or more electrons. This is the reason that the Lithium atom is harder to solve than Helium. This can be seen in the following example. Suppose you have a 3 electron atom with the state: $|1sd; 1su; 2su\rangle$. There are 6 possible permutations of this basis that lead to quantum states. However, under the exchange of any pair of electrons, one will be completely symmetric, one completely anti-symmetric, and the other four will have a mixed symmetry. Thus, not all of the permutations lead to valid solutions, and we need to be more careful about what states we allow in our analysis. This is the motivation for introducing a matrix of Slater Determinates of which we can then use as a basis for our Lithium Hamiltonian.

Because of the Pauli Exclusion Principle it is essential that the wave function for multi-electron atoms be completely antisymmetric under exchange of any two electron pairs. Due to this fact it is common practice to represent the wave functions in an expansion of Slater

Determinates. This method will guarantee that the wave function is antisymmetric, as the Slater Determinate is constructed to satisfy this condition. It is possible to write the Slater Determinate for Lithium as:

$$|||ad; bu; cd||| = \frac{1}{\sqrt{6}}(1 + \mathcal{L} + \mathcal{R})(1 - \hat{P}_{23})|n_1 sd; n_2 su; n_3 su\rangle \quad (3)$$

It should be noted that \hat{P}_{ij} is the exchange operator for electrons i and j , $\mathcal{L} = \hat{P}_{12}\hat{P}_{23}$ is a cyclic left-rotation of the spin orbitals, *i.e.* $\mathcal{L}|a; b; c\rangle = |b; c; a\rangle$, and \mathcal{R} is a cyclic right-rotation, where, $\mathcal{R} = \mathcal{L}^\dagger$. The convention used through out the paper is that the orbital state of the $|d\rangle$ electron is listed first, followed by the states of the two $|u\rangle$ electrons. The term: $(1 + \mathcal{L} + \mathcal{R})(1 - \hat{P}_{23})$ converts a product state into a slater determinate and can thus be called an "antisymmetrizer".

III. MATRIX ELEMENTS OF SLATER DETERMINANTS

The Slater Determinate can be calculated in the following manner [6]:

$$|||ad; bu; cd||| = \det \begin{vmatrix} \phi[a]d(1) & \phi[b]d(1) & \phi[c]d(1) \\ \phi[a]d(2) & \phi[b]d(2) & \phi[c]d(2) \\ \phi[a]d(3) & \phi[b]d(3) & \phi[c]d(3) \end{vmatrix} \quad (4)$$

Here, $|||\psi|||$ is used to denote a Slater Determinate, and $\phi[a]$ is a spatial orbital. From this form of the matrix it is apparent that $\phi[a]$ and $\phi[b]$ or $\phi[a]$ and $\phi[c]$ can be the same spatial orbital function and the determinate will be non-zero, however if $\phi[b] = \phi[c]$, then the determinate will vanish. This can be seen by the spin columns. Columns 2 and 3 have the same spin and thus cannot have the same spatial function if we want a non-zero determinate.

In order to construct our Lithium Hamiltonian, we will expand the wave functions and create a basis made of antisymmetric spin-orbitals using Slater Determinates. In order to construct the Hamiltonian it is essential that we note that the matrix elements of the Hamiltonian with two Slater Determinates can be written as:

$$\langle|||a, b, c|||\hat{H}|||A, B, C||| = \langle a, b, c|\hat{H}|A, B, C\rangle - \langle a, b, c|\hat{H}|A, C, B\rangle \quad (5)$$

Where the second term comes about from the anti-symmetric nature of the wave function.

IV. REPRESENTATION OF THE LI HAMILTONIAN IN A BASIS OF SLATER DETERMINANTS

One of the two key aspects of this analysis was to expand the Hamiltonian in a basis of Slater Determinates. The methodology of this has been previously discussed, and now we will show the actual process and code that was used to achieve this. A sample of the code that was used to calculate the Hamiltonian for Lithium can be seen in Figure 1.

Here are a few notes about notation used in the code. $P_{n, l, zz}$ is the the Legendre polynomial associated with the n th energy level, and state l . zz is the variational parameter as will be discussed in the variational analysis section. The Hamiltonian is of the form discussed in the Introduction. From this analysis, we found the Slater Determinate of the Lithium Hamiltonian using the basis states: $1s^2 2s$, $1s^2 3s$, to be:

$$\text{Slater Determinate for Li} = \begin{bmatrix} -7.05658 & -0.26949 \\ -0.26949 & -7.04538 \end{bmatrix} \quad (6)$$

```

(*H10*) Pn[,1,zz[r_]] := Sqrt[zz] Pn[,1][zz r]

(*H11*) H11a[{n1_, n2_, n3_}, {n4_, n5_, n6_}, zz_, Z_] :=
  D[n3, n6] D[n2, n5] NIntegrate[Pn[1,0,zz[r]] (-1/2) D[r, r] Pn[0,0,zz[r]] - Z/r Pn[0,0,zz[r]]], {r, 0, w}];
H11b[{n1_, n2_, n3_}, {n4_, n5_, n6_}, zz_, Z_] :=
  D[n3, n6] D[n1, n4] NIntegrate[Pn[2,0,zz[r]] (-1/2) D[r, r] Pn[0,0,zz[r]] - Z/r Pn[0,0,zz[r]]], {r, 0, w}];
H11c[{n1_, n2_, n3_}, {n4_, n5_, n6_}, zz_, Z_] :=
  D[n1, n4] D[n2, n5] NIntegrate[Pn[3,0,zz[r]] (-1/2) D[r, r] Pn[0,0,zz[r]] - Z/r Pn[0,0,zz[r]]], {r, 0, w}];
V12[{n1_, n2_, n3_}, {n4_, n5_, n6_}, zz_] :=
  D[n3, n6] NIntegrate[Pn[1,0,zz[r1]] Pn[2,0,zz[r2]] Min[1/r2, 1/r1] Pn[0,0,zz[r1]] Pn[0,0,zz[r2]],
    {r2, 0, w}, {r1, 0, w}];
V13[{n1_, n2_, n3_}, {n4_, n5_, n6_}, zz_] := D[n3, n6] NIntegrate[Pn[1,0,zz[r1]]
  Pn[0,0,zz[r3]] Min[1/r3, 1/r1] Pn[0,0,zz[r1]] Pn[0,0,zz[r3]], {r3, 0, w}, {r1, 0, w}];
V23[{n1_, n2_, n3_}, {n4_, n5_, n6_}, zz_] := D[n1, n4] NIntegrate[Pn[2,0,zz[r2]]
  Pn[0,0,zz[r3]] Min[1/r2, 1/r3] Pn[0,0,zz[r2]] Pn[0,0,zz[r3]], {r2, 0, w}, {r3, 0, w}];

(*H12*) H11d[{n1_, n2_, n3_}, {n4_, n5_, n6_}, zz_, Z_] :=
  H11d[{n1, n2, n3}, {n4, n5, n6}, zz, Z] =
  (H11a[{n1, n2, n3}, {n4, n5, n6}, zz, Z] + H11b[{n1, n2, n3}, {n4, n5, n6}, zz, Z] +
  H11c[{n1, n2, n3}, {n4, n5, n6}, zz, Z] + V12[{n1, n2, n3}, {n4, n5, n6}, zz] +
  V13[{n1, n2, n3}, {n4, n5, n6}, zz] + V23[{n1, n2, n3}, {n4, n5, n6}, zz]) -
  (H11a[{n1, n2, n3}, {n4, n6, n5}, zz, Z] + H11b[{n1, n2, n3},
    {n4, n6, n5}, zz, Z] + H11c[{n1, n2, n3}, {n4, n6, n5}, zz, Z] +
  V12[{n1, n2, n3}, {n4, n6, n5}, zz] + V13[{n1, n2, n3}, {n4, n6, n5}, zz] +
  V23[{n1, n2, n3}, {n4, n6, n5}, zz]);

(*H13*) st11b = Table[{1, 1, 1}, {1, 2, 3}];
(*H14*) {{1, 1, 2}, {1, 1, 3}};

(*H15*) SlaterDet = Quiet[
  Table[H11d[st11b[[j]], st11b[[j]], 3, 3], {j, Length[st11b]}, {j, Length[st11b]}];
SlaterDet // MatrixForm

(*H16*)
{-7.05658 - 0.26949
 -0.26949 - 7.04538}

```

FIG. 1. A sample of the Mathematica code that was used to find the Slater Determinate Matrix in the $1s^2 2s$, $1s^2 3s$ basis

V. VARIATIONAL ANALYSIS OF THE LI $1s^22s$ STATE.

The Variational Principle is the second crucial element of the analysis of the low lying energy states of Lithium. The Variational Principle states that for any guess of the ground state wave function, the energy of that state must be equal to or greater than the actual ground state energy. By using a clever guess for your wave function it is possible to get close to but slightly greater than the actual ground state energy, thus putting an upper limit on the ground state energy. The method that was used to get an upper limit on the ground state energy was to use an adjustable parameter and to minimize the expectation value of our wave function guess, ψ_g with the Hamiltonian, H .

It is reasonable, from the Pauli Exclusion Principle, to expect the ground state wave function of Lithium to be of the $1s^22s$ form. Using this form and the parameter zz in our Slater Determinate we were able to obtain the minimization equation:

$$\frac{5965}{5832}zz + \frac{9}{8}(zz - 6)zz = 0 \quad (7)$$

Solving this equation led to the variational parameter value: $zz = 2.54542$. A physical interpretation for why this value is less than the charge of the nucleus, $Z = 3$, is that the electrons around the nucleus provide a shielding effect of the positive nucleus charge creating an effective charge that is less than what the nucleus actually is.

Using this wave function as the ground state guess with the adjustable parameter, zz , we obtained an upper limit on the ground state energy of Lithium of -7.28906 Ha. This value is 2.52637% different from the NIST value of: -7.47798 Ha [2]. As we add more orbitals into our basis we expect to get a better value for the ground state energy.

The first extra basis state that we chose to include was the $1s^23s$ state. In this case we found the variational parameter to be: $zz = 2.68878$. Note that this is still less than the charge on the nucleus as previously stated. Following the same procedure as with the $1s^22s$ state, we find the ground state energy to be -7.41623 Ha, about 0.825804% different from the NIST value [2]. By including both the $1s^22s$ and $1s^23s$ basis states in our analysis we were able to determine the ground state energy of Lithium to below 1% and make a 3 fold improvement on our value from including just one basis state.

As we include more states in our basis, we expect our value to approach the actual value. A full list of the basis states that we included can be found in Appendix A. We ultimately used 34 basis states to determine our calculated ground state energy of the Lithium atom. We obtained the value: -7.42115 Ha, 0.759904 % different than the listed NIST value of: -7.47798 Ha. The limiting factor on how many basis states we used was how computationally demanding the calculation of the Hamiltonian matrix was. We do expect that the percent difference will decrease with the amount of basis states that

we chose to include, however it is not as simple as just randomly choosing more basis states. Each state does not contribute equally to the energy values. This will be discussed further in the Conclusions section.

VI. QUANTUM DEFECT ANALYSIS OF LI

It is common to assume that the energies of the n th level of most atoms, and especially the alkali-metal atoms, closely follow the semi-empirical formula [6]:

$$E_n = E_\infty - \frac{1}{2(n - \delta)^2} \quad (8)$$

E_∞ would be the energy of the atom if the electron that was most weakly bound was removed, n is the energy level, and δ is the Quantum Defect.

Using a non-linear model fit in Mathematica [4], we were able to obtain a value for the quantum defect given our analysis of the low lying energy levels in Lithium. We obtained the value: $\delta = 0.408504$. The NIST value of the defect is $\delta_{NIST} = 0.401185$, 1.82407% different from our value [2].

It is also possible to find the ionization potential for our analysis and compare to the NIST value. If we subtract the Lithium ground state energy, E_2 , from both sides of the equation for E_n , we can obtain the relationship:

$$IP = E_\infty - E_2 \quad (9)$$

From this we found our ionization potential of Lithium to be 0.196953 Ha. The NIST value is: 0.19814 Ha. Our ionization potential was 0.599975% different than the NIST value [2]. For both of these values we are in the sub 2% accuracy level.

VII. CONCLUSIONS

Through the use of variational analysis and the expansion of the hamiltonian into a basis of Slater Determinates we were able to use undergraduate level quantum mechanics and Mathematica in order to obtain the ground state energy of the Lithium atom to better than 1% of the reported value in NIST. Furthermore, we were able to obtain a value for the quantum defect at a level of better than 2%. We used 34 basis states to achieve this level of uncertainty. As was stated previously we expect our result to get better with an increased number of basis states, however not all states contribute equally to the improvement on the calculated value of the ground state energy. By adding the $1s^23s$ state to the $1s^22s$ state we found a 3 fold improvement on the calculated value. What states we choose to include in our analysis will greatly effect our reported value. The next step in

improvement of this analysis would be to use second order perturbation theory in order to find a constraint on what states contribute most to the accuracy in our calculation of the energy levels of the Lithium atom. Once you have the most influential states you can create a Hamiltonian of those states as the basis, and recalculate using the same method as before. The inclusion of more states will give you a more accurate value, but as you add more states the computational difficulty grows. By using the states in order of their contribution you can find an accurate value for the energy levels based on your computational limitations. We do not go into that analysis here as this was meant to be an exercise in using undergraduate level quantum mechanics to be able to achieve remarkable accuracies.

VIII. APPENDIX A: LIST OF BASIS STATES

A list of the 34 basis states chosen to obtain the final reported value of the ground state energy of Lithium as -7.42115 Ha:

$$\begin{array}{cccccc}
 1, 1, 2 & 1, 1, 3 & 1, 1, 4 & 1, 1, 5 & 1, 1, 6 & \\
 1, 1, 7 & 1, 1, 8 & 1, 1, 9 & 1, 1, 10 & 1, 1, 11 & \\
 1, 1, 12 & 1, 1, 13 & 1, 1, 14 & 1, 1, 15 & 1, 1, 16 & \\
 2, 1, 2 & 2, 1, 3 & 3, 1, 2 & 1, 2, 3 & 2, 1, 4 & \\
 4, 1, 2 & 1, 2, 4 & 2, 1, 5 & 5, 1, 2 & 1, 2, 5 & \\
 2, 1, 6 & 6, 1, 2 & 1, 2, 6 & 2, 1, 7 & 7, 1, 2 & \\
 1, 2, 7 & 3, 1, 4 & 4, 1, 3 & 1, 3, 4 & &
 \end{array} \quad (10)$$

-
- [1] Robert Massé and Thad G. Walker, “Accurate energies of the He atom with undergraduate quantum mechanics”, *Am. J. Phys.* 83, 730 (2015).
 - [2] P.J. Linstrom and W.G. Mallard, Eds., NIST Chemistry WebBook, NIST Standard Reference Database Number 69, National Institute of Standards and Technology, Gaithersburg MD, 20899, doi:10.18434/T4D303
 - [3] P.J. Mohr, D.B. Newell, and B.N. Taylor (2016), “The 2014 CODATA Recommended Values of the Fundamental Physical Constants” (Web Version 7.2). This database was developed by J. Baker, M. Douma, and S. Kotochigova. Available: <http://physics.nist.gov/constants>. National Institute of Standards and Technology, Gaithersburg, MD 20899.
 - [4] Wolfram Research, Inc., *Mathematica*, Version 11.3, Champaign, IL (2018).
 - [5] Townsend, J. S. (2012). *A Modern approach to quantum mechanics*. Mill Valley (Calif.): University Science Books. ISBN: 978-1891389788
 - [6] Woodgate, G. K. (2002). *Elementary atomic structure*. Oxford: Clarendon Press. ISBN-13: 978-0198511564