

Li Project

The goal of this project is to use your knowledge of quantum mechanics to compute many of the low-lying energy levels of the Li atom. Since the Li atom has 3 electrons, you will learn how to construct 3-electron wavefunctions that satisfy the Pauli exclusion principle. You will use both variational methods and a basis set expansion to get your final results. You will learn about Slater determinants and exchange operators. You will compare your calculations to experiment, and you should be able to attain accuracies for most of the properties of Li to better than 1% error, and some to less than 0.1% error. Quantum mechanics really works!

To get started, you will first solve the simpler problem of the 2-electron Li^+ ion. This simpler calculation is very similar to that of the He atom, written up by a 449 alumnus (Robert Massé) in the paper “Accurate energies of the He atom with undergraduate quantum mechanics”, Am. J. Phys. 83, 730 (2015), which you will need to read carefully. To the methods there, you will add a variational calculation for the ground state, then use a basis set founded on that variational calculation to both improve the ground state energy a bit, and to get the energies of some of the low-lying excited states.

The addition of the third electron in the neutral Li atom adds some complexity to the problem. For Li^+ it is sufficient to use a non-symmetrized basis set; the exchange symmetry of the Hamiltonian gives spatial eigenfunctions that are either symmetric or anti-symmetric on interchange, and these are easily identified. For the 3-electron problem, one cannot be so casual and explicitly anti-symmetrized wavefunctions are necessary. To this end, you will construct Slater determinants that satisfy this requirement, and use your knowledge of commutation relations to simplify the calculation of matrix elements of the Hamiltonian. You will again first perform a variational calculation of the ground state energy, then use a related basis set expansion to get the excited states. You will then use a quantum defect analysis of your results to deduce the ionization energy of Li, to an accuracy better than 0.1%.

You will do the above calculations in small 2 or 3 person teams. To ensure proper progress, there will be intermediate due dates for various parts of the project. Once you complete your calculations, each student will write a short (3-5 journal pages) paper on your work. There will be a prize for the best paper and there is also the potential to submit the paper, suitably revised, for publication in a refereed journal.

Li^{++}

The Hamiltonian for the single-electron Li^{++} atom is just like hydrogen, but with a charge of 3 on the nucleus. In atomic units

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

with $Z = 3$ for the Li nucleus.

1) Show that the radial eigenfunctions of \hat{H}^{++} are $P_{nl}^{++}(r) = N(Z) P_{n,l}(Zr)$, where $P_{n,l}(r)$ are the eigenfunctions of hydrogen. Find the normalization factor $N(Z)$. Find the energies.

Li⁺

The Hamiltonian for the two-electron Li⁺ ion is (with $Z = 3$)

$$\hat{H}^+ = \hat{H}^{++}(1) + \hat{H}^{++}(2) + \frac{1}{r_{12}} = \hat{H}_0 + V_{12} = -\frac{1}{2} \nabla_1^2 - \frac{Z}{r} - \frac{1}{2} \nabla_2^2 - \frac{Z}{r} + \frac{1}{r_{12}} \quad (2)$$

We are going to restrict our considerations to states of total angular momentum $L = 0$, which we assume is made of only of s-type single-electron orbitals $P_{n0}^{++}(r) = P_n^z(r) = N(z) P_{n,0}(zr)$. Here $z \neq Z$ is a parameter we will use for a variational calculation below. The basis states we will denote simply as $|n_1; n_2\rangle$, whose representation in position space is

$$\langle r_1; r_2 | n_1; n_2 \rangle \equiv P_{n_1}^+(r_1) P_{n_2}^+(r_2).$$

2) Show that the matrix elements of \hat{H}^+ are

$$\langle n_1; n_2 | \hat{H}^+ | n_3; n_4 \rangle = \langle n_1 | \hat{H}^{++} | n_3 \rangle \delta_{n_2, n_4} + \langle n_2 | \hat{H}^{++} | n_4 \rangle \delta_{n_1, n_3} + \langle n_1; n_2 | V_{12} | n_3; n_4 \rangle \quad (3)$$

Write Mathematica routines to calculate (analytically) $\langle n_1 | \hat{H}^{++} | n_3 \rangle$ and $\langle n_1; n_2 | V_{12} | n_3; n_4 \rangle$; check your results against the Massé paper for He.

You are now ready to do a simple variational calculation of the ground state energy of Li⁺. For your variational wavefunction, pick $P_{n_1}^z(r_1) P_{n_2}^z(r_2)$, keeping z to be your variational parameter.

3) Minimize the ground-state ($1s^2$) energy with respect to z , and compare your results to the NIST experimental energy. Make a physical argument why $z < Z$.

Now make a somewhat more sophisticated calculation. Your variational wavefunction for the $1s^2$ state should be a pretty good representation. So use the set of functions $P_{n_1}^z(r_1) P_{n_2}^z(r_2)$ as a basis, with z chosen as the result of your variational calculation. Make a list of the 17 lowest energy states and use those as a basis. Even though all the 17^2 integrals can be done analytically, in the interest of time it is useful to do them numerically.

4) Use your 17 state basis to construct the Hamiltonian for Li⁺, and find the energy eigenvalues. How much better is your $1s^2$ energy?

5) Looking at your eigenvectors, which ones are singlets and which ones are triplets? Calculate the $1s2s$ singlet and triplet energies, and compare to experiment. Also compare the $1s2s$ singlet-triplet splitting to experiment.

Li

The Hamiltonian for the three-electron Li atom is

$$\hat{H} = \hat{H}^{++}(1) + \hat{H}^{++}(2) + \hat{H}^{++}(3) + \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}} = \hat{H}_0 + V_{12} + V_{13} + V_{23} \quad (4)$$

The Hamiltonian commutes with the exchange operators P_{12} , P_{13} , P_{23} . But these operators do not commute with each other, so the eigenvectors can be chosen to be eigenvectors of one of the exchange operators but not (necessarily) all. But the Pauli exclusion principle says that the valid eigenvectors must be eigenvectors of all three exchange operators, with eigenvalue -1 for each? How does that work?!?

As with Li^+ , the fact that the Hamiltonian contains no spin operators does not mean that the spin has no effect on the energy. Again, the requirement of anti-symmetry of the wavefunction on interchange of any pair of atoms will strongly restrict the possible allowed states and energies of the Hamiltonian. The Hamiltonian will have many mathematically allowed states that violate the Pauli exclusion principle.

Putting aside these extremely important issues for the moment, we define some notation. The three electrons have spin-1/2, so the eigenfunctions of \hat{H} will have both spatial and spin parts. We will denote a single electron spin-orbital by $\langle \bar{r} | a \rangle = \varphi[a] \chi[a]$. Here $\varphi[a]$ is a generic orbital (spatial) function, usually equal to one of the $P_n^{++}(r) Y_{lm} / r$, and $\chi[a]$ is either $|u\rangle$ or $|d\rangle$, depending on the electron's spin-projection along the z-axis. A 3-electron spin-orbital will be denoted $\langle \bar{r}_1 \bar{r}_2 \bar{r}_3 | a; b; c \rangle = \varphi[a, b, c] \chi[a, b, c]$ where $\varphi[a, b, c] = \varphi[a] \varphi[b] \varphi[c]$ and $\chi[a, b, c]$ might be $|u u d\rangle$ for example. Electron #1 is always listed first, followed by 2 and 3. As a specific example, a $1s^2 2s$ basis function would be

$$\langle \bar{r}_1 \bar{r}_2 \bar{r}_3 | 1s d; 1s u; 2s u \rangle = \varphi[1, 1, 2] d u u = P_1^{++}(r_1) \frac{Y_{00}}{r_1} P_1^{++}(r_2) \frac{Y_{00}}{r_2} P_2^{++}(r_3) \frac{Y_{00}}{r_3} d \otimes u \otimes u.$$

The exchange operators are defined by, for example

$$\hat{P}_{12} |a; b; c\rangle = |b; a; c\rangle \quad (5)$$

Products of exchange operators produce cyclic permutations of the state. For example, a left-rotation is produced by the operator

$$\hat{\mathcal{L}} |a; b; c\rangle = \hat{P}_{13} \hat{P}_{23} |a; b; c\rangle = \hat{P}_{13} |a; c; b\rangle = |b; c; a\rangle \quad (6)$$

while a right-rotation, equivalent to two left-rotations, is

$$\hat{\mathcal{R}} |a; b; c\rangle = \hat{P}_{23} \hat{P}_{13} |a; b; c\rangle = \hat{P}_{23} |c; b; a\rangle = |c; a; b\rangle = \hat{\mathcal{L}}^2 |a; b; c\rangle \quad (7)$$

6) Calculate $[\hat{P}_{23}, \hat{P}_{13}]$. Give your answer in terms of $\hat{\mathcal{L}}$ and $\hat{\mathcal{R}}$. Show that $[\hat{\mathcal{L}}, \hat{H}] = [\hat{\mathcal{R}}, \hat{H}] = 0$.

Show that $\hat{\mathcal{L}}^3 = \mathbb{1}$ and $\hat{\mathcal{L}}^\dagger = \hat{\mathcal{R}}$. Are $\hat{\mathcal{L}}^\dagger$ and $\hat{\mathcal{R}}$ unitary, Hermitian, or what?

7) Prove that if $|\psi\rangle$ is an eigenvector of \hat{P}_{12} and \hat{P}_{23} with eigenvalue -1, it is also an eigenvector of \hat{P}_{13} with eigenvalue -1. One way to do this is to calculate $\hat{Q} = \hat{P}_{23} \hat{P}_{12}$. Show that $\hat{Q} |\psi\rangle = |\psi\rangle$. Then $\hat{P}_{13} |\psi\rangle = \hat{P}_{13} \hat{Q} |\psi\rangle = \dots$

Slater Determinants and the Pauli Exclusion Principle

See the handout on Slater determinants for an important discussion of what they are and their significance for constructing an appropriate set of 3-electron basis functions.

For Li we have 3 spin-1/2 electrons, so the total orbital angular momentum $\bar{L} = \bar{L}_1 + \bar{L}_2 + \bar{L}_3$ can be 1/2 or 3/2. We know that the lowest state of Li^+ has $S = 0$, $L = 0$, so when we add the 3rd electron we expect that the spin quantum number will be $S = 1/2$ (a “doublet”) with $L = 0$ still. Since $S = 1/2$ then $m_S = \pm 1/2$. The only way to make $m_S = 1/2$ is for one of the electrons to be in the $|d\rangle$ state, and other two $|u\rangle$. We make the convention that we list the orbital state of the $|d\rangle$ electron first, then the orbital states of the two $|u\rangle$ electrons. The orbital states of the $|u\rangle$ must always be different, or the Slater determinant would vanish.

8) Show that a Slater determinant for Li can be written as

$||a d, b u, c u|| = \frac{1}{\sqrt{6}} (1 + \mathcal{L} + \mathcal{R}) (1 - \hat{P}_{23}) |a d, b u, c u\rangle = \frac{1}{\sqrt{6}} \mathcal{A} |a d, b u, c u\rangle$. We might call the operator \mathcal{A} an “antisymmetrizer” as it converts a product state into a Slater determinant.

We are now ready to start considering how to calculate the matrix elements of the Hamiltonian. For two spin-orbitals $|a, b, c\rangle$ and $|A, B, C\rangle$ the Hamiltonian matrix elements have these properties:

1. The ordering of the spin-orbitals is irrelevant, as long as the associations $a \leftrightarrow A, b \leftrightarrow B, c \leftrightarrow C$ are preserved. This follows from $[\hat{H}, \hat{P}_{ij}] = 0$.
2. The spin parts of the orbitals must be the same, $\chi(a) = \chi(A)$ etc. The Hamiltonian is a identity operator for spin. This implies, perhaps non-intuitively, that electrons of opposite spins “do not interact”.
3. Because the Hamiltonian consists only of 1-electron and 2-electron operators, its matrix elements vanish unless $a \equiv A || b \equiv B || c \equiv C$ is true.

9) Show that the matrix elements of the Hamiltonian with two Slater determinants can be simplified to $\langle ||a, b, c|| \hat{H} ||A, B, C|| \rangle = \frac{1}{6} \langle a d, b u, c u | \mathcal{A}^\dagger \mathcal{A} \hat{H} | A d, B u, C u \rangle$, and that $\mathcal{A}^\dagger \mathcal{A} = 3 (1 - \hat{P}_{23}) \mathcal{A}$

10) Show further that when we evaluate the various inner products of the spins we get

$$\begin{aligned} \frac{1}{6} \langle a d, b u, c u | \mathcal{A}^\dagger \mathcal{A} \hat{H} | A d, B u, C u \rangle &= \frac{1}{2} \langle a d, b u, c u | (1 - \hat{P}_{23})^2 \hat{H} | A d, B u, C u \rangle \\ &= \langle a, b, c | \hat{H} | A, B, C \rangle - \langle a, b, c | \hat{H} | A, C, B \rangle \end{aligned}$$

You will want to focus on the spins.

This last result,

$$\langle ||a, b, c|| \hat{H} ||A, B, C|| \rangle = \langle a, b, c | \hat{H} | A, B, C \rangle - \langle a, b, c | \hat{H} | A, C, B \rangle \quad (8)$$

tells us how to construct the Hamiltonian for our 3-spin system from just the spatial orbitals. The first (“direct”) term we would’ve guessed, but the second (“exchange”) term is a non-intuitive consequence of the anti-symmetry of the wavefunction.

11) Extend your code for Li^+ to calculate the Slater determinant matrix elements for the Li Hamiltonian.

Variational Energy of Li

You are now ready to make a variational calculation of the ground state energy of Li. According to the Pauli exclusion principle, the lowest energy wavefunction will likely be of the “1s 1s 2s” form $\langle r_1 r_2 r_3 | 1 s; 1 s; 2 s \rangle = P_1^z(r_1) P_1^z(r_2) P_2^z(r_3)$ with again z being an adjustable parameter.

11) Using a 1s1s2s wavefunction with variable z , find an upper limit on the ground state energy of the Li atom, and compare to experiment.

13) Thad got about 2.5% error, so let's try to improve by adding a 1s1s3s orbital to the mix. Construct the 2x2 Hamiltonian for this basis, find the energies, and minimize the lowest energy. Your answer should significantly improve.

Now is probably a good time to use a fixed value for z , the value of which should be quite close to what you used for Li^+ . The rest of the project will be done using this particular value of z .

14) Switch to doing the integrals numerically, and add a few more 1s1sns orbitals, maybe even a few 2s1sns. How much does the answer improve?

Quantum Defect Analysis

You may have hit the wall on the precision of the $1 s^2 2 s$ state, but what about the excited states? Most experiments on atoms measure not the absolute energies, but the energy differences between the various states.

14) Compare your $1 s^2 3 s - 1 s^2 2 s$ energy difference with experiment.

It is well known the energy levels for most atoms, and the alkali-metal atoms in particular, closely obey the semi-empirical formula

$$E_n = E_\infty - \frac{1}{2(n-\delta)^2} \quad (9)$$

where δ is called the “quantum defect” and E_∞ is the total energy of the atom when the most weakly bound electron is removed. For Li, E_∞ would be the ground-state energy of Li^+ and $n = 2, 3, 4, \dots$ is the principal quantum number of the outer electron. Subtracting the Li ground state energy E_2 from both sides of the equation gives

$$E_n - E_2 = \text{IP} - \frac{1}{2(n-\delta)^2} \quad (10)$$

where $\text{IP} = E_\infty - E_2$, the ionization potential, is the difference between the ground state energies of Li^+ and Li, and is therefore the amount of energy required to remove one electron from the Li atom.

15) From the NIST tables, plot the Li energies vs n and deduce the value of the quantum defect.

You will get the most accurate value of δ if you define an effective quantum number

$n^* = [2(E_\infty - E_n)]^{-1/2}$ and plot n^* vs n . Use a Mathematica fitting function such as NonLinearModelFit to find δ .

16) Now repeat, but with your calculated energy levels. Fit to find E_∞ and from that deduce your ionization potential and quantum defect and compare to experiment.