

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 variation calculation below. The basis states we will denote simply as $|n_1; n_2\rangle$, whose representation in position space is $\langle r_1; r_2 | n_1; n_2 \rangle \equiv P_{n_1 n_2}^+(r_1, r_2) = P_{n_1}^z(r_1) P_{n_2}^z(r_2)$.

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 singlet-triplet splitting to experiment.