

Energies of the Lithium Atom Using Undergraduate Quantum Mechanics

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With three electrons the Lithium atom can be used as a simple model of how the energy levels of an atom must obey the Pauli Exclusion Principle. Through undergraduate level quantum mechanics and Mathematica we were able to calculate the energies of the low lying states of Lithium to *** percent. The method included using variational analysis and representing the hamiltonian of Li in a basis of Slater Determinate. A quantum defect analysis was also performed and the defect was found to be ***, *** percent different than the calculate NIST value [2].

The Lithium atom has 3 electrons and as such has a special consideration that needs to be taken into account that would not be necessary with two or less electrons, namely the Pauli Exclusion Principle. Despite this complication, Lithium has the benefit of being the simplest and lightest atom to consider that has this added constraint that needs to be taken into account when modeling the wave functions. Here we present an analysis of the low lying energy levels of the Lithium atom using Quantum Mechanics accessible at an undergraduate level as well as Mathematica software. Using the variational principle and representing the hamiltonian in a basis of slater determinates we were able to obtain the energies to *****.

It is typical in undergraduate mechanics courses to talk about the wave functions and energy levels of the Hydrogen and Helium atoms...

For the 2 electron He atom,... Thus the energy levels of 2-electron atoms can be calculated in a straightforward manner using a simple product basis [1].

For this project we want to calculate a few of the low lying energy states in our 3 electron Lithium.

It should 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].

I. THE PAULI EXCLUSION PRINCIPLE

**Add Slater determinate constructed to be antisymmetric

The Pauli Exclusion Principle states that the wave function 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 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 introducing Slater Determinates which we will expand our Lithium Hamiltonian in a basis of.

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. It is possible to write the Slater Determinate for Lithium as:

$$||ad; bu; cd|| = \frac{1}{\sqrt{6}}(1 + \mathcal{L} + \mathcal{R})(1 - \hat{P}_{23})|n_1sd; n_2su; n_3su\rangle \quad (1)$$

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".

II. MATRIX ELEMENTS OF SLATER DETERMINANTS

The Slater Determinate can be calculated in the following manner:

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