Energies of the Li Atom Using Undergraduate Quantum Mechanics*

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This paper demonstrates the calculation of the low-lying energies levels of the Li atom. Given that the Li atom has 3 electron, an appropriate wavefunction can be contrcuted based on the Pauli exclusion principle. The matrix elements of the Hamiltonian of the Li atom will be determined from the components of the Slater determinant. Besides, the variational analysis of the Li $1s^22s$ states helps restrict the limit of the ground state energy. The Hamiltonian of the Li atom can then be represented through the low-lying energy states. Finally, a quantum defect analysis helps study on the excited states energy.

The Li atom, with 3 electrons, is the lightest and simplest atom whose energy levels are radically constrained by the Pauli Exclusion Principle. For the 2 electron He atom, the matrix diagonalization can be used to evaluate the energies of $1s2s$ singlet and triplet states. Thus the energy levels of 2-electron atoms can be calculated in a straightforward manner using a simple product basis [1].

To begin, we can obtain an approximate form of the wavefunction for the Li atom by considering the Hamiltonian of the Li ions. The Hamiltonian of the Li atom can be written in the form

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

Here $\hat{H}^{++}$ denotes the Hamiltonian for the Li^{++} ion and Z represents the atomic number. After the normalization, the wavefunction can be written as

$$P^{++}_{n,l}(r) = \sqrt{zz}P_{n,l}(Zr) \tag{2}$$

Here $P^{++}_{n,l}(r)$ is the radial wavefunction for the Li^{++} ion and correspondingly the $P_{n,l}(r)$ is that for the Li atom, where zz is a variational parameter that can be alternated when the particular energy states are calculated.

In the following I will present a calculation of the low-lying energy levels of the Li atom using a variationally chosen basis of Slater determinants.

I. THE PAULI EXCLUSION PRINCIPLE

A naive version of the Pauli principle, namely that the three electrons must have unique quantum numbers, erroneously leads to the conclusion that the 6 permutations of the state $|1sd; 1su; 2su\rangle$ would be all be valid quantum states. . . The solution to the Li Hamiltonian in such a basis results in one solution that is completely symmetric upon exchange of any pair of electrons, one totally anti-symmetric solution, and four solutions of mixed exchange symmetry.

The full Pauli principle requires that only the totally anti-symmetric solution is valid. This solution is compactly represented by the Slater determinant

$$\begin{aligned}&|\|ad; bu; cd\|\rangle = \\ &\frac{1}{\sqrt{6}}(1 + \mathcal{L} + \mathcal{R})(1 - P_{23})|n_1sd; n_2su; n_3su\rangle\end{aligned} \tag{3}$$

Here P_{ij} is the exchange operator for electrons i and j, $\mathcal{L} = P_{12}P_{23}$ is a cyclic left-rotation of the spin orbitals, *i.e.* $\mathcal{L}|a; b; c\rangle = |b; c; a\rangle$, and $\mathcal{R} = \mathcal{L}^\dagger$ is a cyclic right-rotation. With the notations defined, we are able to prove that if $|\psi\rangle$ is an eigenvector of P_{12} and P_{23} with eigenvalue -1, it is also an eigenvector of P_{13} with eigenvalue -1. Let $\mathcal{Q} = P_{23}P_{12}$. With $P_{12} = -|\psi\rangle$ and $P_{23} = -|\psi\rangle$, it follows that

$$\begin{aligned}&Q|\psi\rangle = \\ &P_{23}P_{12}|\psi\rangle = P_{23}(P_{12}|\psi\rangle) = \\ &P_{23}(-|\psi\rangle) = -(P_{23}|\psi\rangle) = -(-|\psi\rangle) = |\psi\rangle)\end{aligned} \tag{4}$$

The above proof shows that given the exchange operators P_{12}, P_{13} and P_{23} which commute with the Hamiltonian, all of their eigenvectors are also valid to be the eigenvectors of the Hamiltonian without violating the Pauli exclusion principle, with eigenvalues -1 for each. And with such a verification, the method to calculate the matrix elements for the Slater determinant for the Li Hamiltonian can be constructed.

II. MATRIX ELEMENTS OF SLATER DETERMINANTS

From the equation (1), we are able to derive a general method to calculate the matrix elements for Li Hamiltonian. Recall that $\mathcal{L} = P_{12}P_{23}$ is a cyclic left-rotation of the spin orbitals and $\mathcal{R} = \mathcal{L}^\dagger$ is a cyclic right-rotation; it follows that

* A footnote to the article title

$$|||ad;bu;cd||\rangle = \tag{5}$$

$$\frac{1}{\sqrt{6}}(1+\mathcal{L}+\mathcal{R})(1-P_{23})|n_1sd;n_2su;n_3su\rangle = \tag{6}$$

$$\frac{1}{\sqrt{6}}(|ad,bu,cd\rangle + |bu,cu,ad\rangle + |cu,ad,bu\rangle - \tag{7}$$

$$|ad,cu,bu\rangle - |cu,bu,ad\rangle - |bu,ad,cu\rangle) = \tag{8}$$

$$\frac{1}{\sqrt{2}}\mathcal{A}|ad,bu,cd\rangle \tag{9}$$

Here the operator A is considered as an "antisymmetrizer" as it converts a product state into a Slater determinant. We can further show that

$$\begin{aligned}
&\frac{1}{6}\langle ad,bu,cd|\mathcal{A}^\dagger\mathcal{A}H|ad,bu,cd\rangle = \\
&\frac{1}{2}\langle ad,bu,cd|(1-P_{23})^2H|Ad,Bu,Cu\rangle = \\
&\langle a,b,c|H|A,B,C\rangle - \langle a,b,c|H|A,C,B\rangle
\end{aligned} \tag{10}$$

Here both $|a,b,c\rangle$ and $|A,C,B\rangle$ are the spin-orbitals of Li Hamiltonian. Therefore, the Hamiltonian of the 3-spin system can constructed from the spatial orbitals. Fig.1 shows the calculation in MATHEMATICA to obtain the Slater determinant matrix elements for the Li Hamiltonian. The first line gives the radial eigenfunction which is also used by the Li ions, where zz represents a variational parameter which can be determined by variational analysis for the Li atom in a particular state; the variational analysis of the Li $1s^22s$ is shown later in the part III. The lines in the second box indicates the Hamiltonian and the potential terms for the 3-spin system from the spatial orbits. The line in the third box gives a total Hamiltonian. By applying this Hamiltonian to $1s^22s$ and $1s^23s$ states, we obtain the first $2*2$ matrix elements for the Slater determinant.

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

A variational calculation of the ground state energy of Li can be realized through the MATHEMTICA coding shown in the previous section. According to the Pauli exclusion principle, it is the most possible to write the lowest energy wavefunction as $\langle r_1,r_2,r_3|1s;1s;2s\rangle = {P_1}^z(r_1){P_2}^z(r_2){P_3}^z(r_3)$, where z is an adjustable parameter.

The steps of the calculation follow the convention of the variational method. First, an expression for the Li $1s^22s$ state with respect to the variational parameter zz can be found by applying the method to calculation the matrix elements to the Li $1s^22s$ state. By starting from the assumption that $E_n \leq E_0$, with E_0 the exact ground-state energy. Thus for any state,

```
P_{n_,l_,zz_}[r_] := √zz P_{n,l}[zz r]
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H11a[{n1_, n2_, n3_}, {n4_, n5_, n6_}, zz_, Z_] :=
  δ_{n3,n6} δ_{n2,n5} NIntegrate[P_{n1,0,zz}[r] (-1/2 ∂_{r,r} P_{n4,0,zz}[r] - Z/r P_{n4,0,zz}[r]), {r, 0, ∞}];
H11b[{n1_, n2_, n3_}, {n4_, n5_, n6_}, zz_, Z_] :=
  δ_{n3,n6} δ_{n1,n4} NIntegrate[P_{n2,0,zz}[r] (-1/2 ∂_{r,r} P_{n5,0,zz}[r] - Z/r P_{n5,0,zz}[r]), {r, 0, ∞}];
H11c[{n1_, n2_, n3_}, {n4_, n5_, n6_}, zz_, Z_] :=
  δ_{n1,n4} δ_{n2,n5} NIntegrate[P_{n3,0,zz}[r] (-1/2 ∂_{r,r} P_{n6,0,zz}[r] - Z/r P_{n6,0,zz}[r]), {r, 0, ∞}];
V12[{n1_, n2_, n3_}, {n4_, n5_, n6_}, zz_] := δ_{n3,n6} NIntegrate[
    P_{n1,0,zz}[r1] P_{n2,0,zz}[r2] Min[1/r2, 1/r1] P_{n4,0,zz}[r1] P_{n5,0,zz}[r2], {r2, 0, ∞}, {r1, 0, ∞}];
V13[{n1_, n2_, n3_}, {n4_, n5_, n6_}, zz_] := δ_{n2,n5} NIntegrate[
    P_{n1,0,zz}[r1] P_{n3,0,zz}[r3] Min[1/r3, 1/r1] P_{n4,0,zz}[r1] P_{n6,0,zz}[r3], {r3, 0, ∞}, {r1, 0, ∞}];
V23[{n1_, n2_, n3_}, {n4_, n5_, n6_}, zz_] := δ_{n1,n4} NIntegrate[
    P_{n2,0,zz}[r2] P_{n3,0,zz}[r3] Min[1/r2, 1/r3] P_{n5,0,zz}[r2] P_{n6,0,zz}[r3], {r2, 0, ∞}, {r3, 0, ∞}];
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```
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]);
```

```
st11b = Table[{1, 1, i}, {i, 2, 3}]

{{1, 1, 2}, {1, 1, 3}}
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```
SlaterDet =
 Quiet[Table[H11d[st11b[[i]], st11b[[j]], 3, 3], {i, Length[st11b]}, {j, Length[st11b]}]];
SlaterDet // MatrixForm

( -7.05658  -0.26949 )
( -0.26949  -7.04538 )
```

FIG. 1. The calculation in MATHEMATICA to obtain the Slater determinant matrix elements for the Li Hamiltonian. An executable and annotated version is available electronically (Ref.)

$$E_0 \leq \langle\psi|\hat{H}|\psi\rangle = \langle E\rangle \tag{11}$$

With choosing a trial state with the variational parameters, $P_{n,l}(r) = \sqrt{zz}P_{n,l}(Zr)$, $\langle\psi|\hat{H}|\psi\rangle$ can be then calculated.

Second, the value of zz that minimizes the energy can be calculated by letting the first derivative of the expression equal to 0, i.e. $\frac{\partial\langle E_{1s,1s,2s}\rangle}{\partial zz} = 0$, regarding to the energy states we are interested in. Fig.2 shows a MATHEMATCA calculation based on the coding we obtained in Fig.1; $zz = 2.54542$ is then obtained.

Third, after plugging in the experimental values for Li atom and writing result in the atomic units, it turns out that the upper limit on the ground state energy of the Li atom approximately equals to -7.28906 Hartrees. The last line of Fig.2 shows the step to get this value.

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

V. QUANTUM DEFECT ANALYSIS OF LI

VI. CONCLUSIONS

```
ϵ0Li = H12d[{1, 1, 2}, {1, 1, 2}, zz, 3]
ϵ0Li // N
```

$$\frac{5965\,zz}{5832} + \frac{9}{8}(-6 + zz)\,zz$$

```
1.02281 zz + 1.125 (-6. + zz) zz
```

$$\text{Solve}\left[\partial_{zz}\left(\frac{5965\,zz}{5832} + \frac{9}{8}(-6 + zz)\,zz\right) == 0,\ zz\right] \text{ // N}$$

```
{{zz → 2.54542}}
```

$$\text{Eval12} = \frac{5965 \times 2.54541990550221\grave{}}{5832} + \frac{9}{8}(-6 + 2.54541990550221\grave{})\,2.54541990550221\grave{}$$

```
-7.28906
```

FIG. 2. The calculation based on the variational principle, where the variable H12d is just the H11d given in Fig.1. An executable and annotated version is available electronically (Ref.)

[1] Robert Massé and Thad G. Walker, "Accurate energies of the He atom with undergraduate quantum mechanics", Am. J. Phys. 83, 730 (2015).