Using scattering theory to calculate the ground state energy of lithium atom

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Abstract. The problem of bound states of atoms with many electrons does not have an analytic solution; therefore, standard methods of approximation are utilized to solve it, and among them, we can find the variational method, the perturbation method and the Hartree Fock method. Said methods may be very difficult to implement and may take a great amount of computational time, even when they are applied to the lithium atom. An alternative method that is considerably easier to implement is proposed in this paper. This involves considering the Hamiltonian for the lithium atom as a collision between an electron and an ionized lithium atom; in this way, the energy of the lithium atom is the sum of energies of a helium atom (with nuclear charge Z = 3) and the energy that an electron needs to be bound to an ionized lithium atom in a collision process. The Quantum Collision Theory under the focus of Jost function was used to calculate the bound state energies of one electron with an ionized lithium atom. Using this approach, we calculated the ground state energy of lithium atom with an error with respect to the experimental value of 0.3%. This error is very low; therefore, the proposed method produces very good results and it can be taken as basis to study atoms with more electrons. Hopefully, in the future, this method could be part of quantum physics books because it is a novel method to observe the formation of atoms.

1. Introduction

The problem of bound states of atoms with many electrons is that it does not have an analytic solution; therefore, methods of approximation are utilized. The most common ones are the variational method, the perturbation method, the Hartree Fock method, among others. However, said methods may be very difficult to implement since integrals with many terms must be solved, even for atoms with a few electrons, such as the helium atom (with atomic number Z = 2) where corrections need to be applied up to the twenty-first order (for the perturbation method), or taking functions of proof with 1078 terms (for the variational method), if good results need to be obtained. For the lithium atom, Yan and Drake calculated the ground state energy with an accuracy of 10^{-10}, but using multiple basis sets in Hylleraas coordinates.

When the level of difficulty of the method decreases, the results are not very good; for example, when the perturbation method is used up to the first order, the ground state energy value obtained is -192 eV, whereas the experimental value is -203.5 eV. That is, we have an error of 5.7% and if the variational method is applied using as function of proof the Slater determinant, a ground state energy value of -201.2 eV is obtained, which represents an error of 1.1%. For this reason, the main objective of this work is proposing a method which is easy to...
apply and that has low-error probability to calculate ground state energy of the lithium atom. To accomplish this objective, the Quantum Collisions Theory was used.

2. Theory
The Quantum Collisions Theory or Scattering Theory is frequently used to calculate the cross sections which are originated when a particle is scattered by a target, but it is possible to use it to study bound states \[7,8\] when the Jost function is taken in account. In the literature, the majority of studies that have used the Jost function are those that deal with scattering and resonance \[9–13\]. On the other hand, there are few methods which allow to calculate it \[14,15\]. The method proposed in \[16\] was chosen in this work to calculate the Jost functions, i.e., the Equation (1) was solved.

\[
F_L''(k, r) - \left[ U'(r) + 2 \frac{h_L^+(kr)}{h_L(kr)} \right] F_L'(k, r) - U(r) F_L(k, r) = 0
\] (1)

In Equation (1), \( U(r) \) represents the interaction between an incident particle, which has angular momentum \( L \) and wave number \( k \), with a target; \( r \) is the distance between the particles; \( h_L^+(kr) \) are the Hankel functions and \( F_L(k, r) \) are named as the Jost solutions. The quotation marks mean to derive with respect to \( r \). It is possible to calculate the Jost functions \( f_L(k) \) by means of Equation (2), after that the Equation (1) is solved.

\[
f_L(k) = \lim_{r \to \infty} F_L(k, r)
\] (2)

On the other hand, we can calculate the energies of the bound states by means of \( E = \frac{k^2 \hbar^2}{2m} \), where \( m \) is the reduced mass of the system, and the values of \( k \) satisfy \( \text{Im}(k) > 0 \) and \( \text{Re}(k) = 0 \) and for which \( f_L(k) = 0 \).

3. method
Lithium is an alkaline atom that can be considered as a system formed by: (a) a core which is constituted by a nucleus and two electrons that are strongly bound to it; (b) a valence electron which largely determines the physical and chemical properties of the atom. Then it can be said that the 1s electrons are more bound to the nucleus than the 2s electron. Therefore, it can be assumed that the valence electron moves under the combined effect of the nucleus and the two 1s electrons. Now the following can be assumed: the electrons of the core have the same charge distribution for all states of the valence electron and, therefore, the spectrum of energies of the valence electron when it moves in the potential created by the core can be calculated, i.e, the lithium atom is being modeled from a collision of one electron (valence electron) with an ionized lithium atom (core).

On the other hand, the electronic Hamiltonian in atomic units for a lithium atom is given in Equation (3) (see \[2\]),

\[
\hat{H} = -\frac{1}{2} \nabla^2_{r_1} - \frac{1}{2} \nabla^2_{r_2} - \frac{1}{2} \nabla^2_{r_3} - \frac{3}{r_1} - \frac{3}{r_2} - \frac{3}{r_3} + \frac{1}{r_{12}} + \frac{1}{r_{13}} + \frac{1}{r_{23}},
\] (3)

where the first, second and third term correspond to the kinetic energies of electrons; the fourth, fifth and sixth term are the electron-nucleus interactions and the last ones are the electron-electron interactions. Now, the Hamiltonian in Equation (3) can be written as \( \hat{H} = \hat{H}^0 + \hat{H}^1 \), where \( \hat{H}^0 \) and \( \hat{H}^1 \) are defined according to Equation (4) and Equation (5).

\[
\hat{H}^0 = -\frac{1}{2} \nabla^2_{r_1} - \frac{1}{2} \nabla^2_{r_2} - \frac{3}{r_1} - \frac{3}{r_2} + \frac{1}{r_{12}}
\] (4)
\[ \hat{H}^1 = -\frac{1}{2} \nabla^2 r_3 - \frac{3}{r_3} + \frac{1}{r_{13}} + \frac{1}{r_{23}} \]  

(5)

In Equation (4), \( \hat{H}^0 \) represents the Hamiltonian of an ionized lithium atom with a ground state energy equal to \( E^0 = -7.279913387 \) (in atomic units) [2]. While from Equation (5), \( \hat{H}^1 \) can be interpreted as the collision of one electron with a nucleus (of \( Z = 3 \)) and the other electrons. In order to find the effective potential that the valence electron experiments due to the interactions with the nucleus and with the charge distribution originated by the other electrons, we consider the time-independent Schrodinger equation, Equation (6).

\[ \hat{H} \Psi(r_1, r_2, r_3) = E \Psi(r_1, r_2, r_3) \]  

(6)

The wave function in Equation (5) may be written as \( \Psi(r_1, r_2, r_3) = \phi_{1s}(r_1)\phi_{1s}(r_2)\phi_{nL}(r_3) \), in accordance with the explanation given in the first paragraph of this section. Replacing the wave function in Equation (6) and after projecting over the ground state of \( \hat{H}_0 \), have Equation (7) and Equation (8).

\[ \int \int \phi_{1s}(r_1)\phi_{1s}(r_2)(\hat{H}^0 + \hat{H}^1)\phi_{1s}(r_1)\phi_{1s}(r_2)\phi_{nL}(r_3)d^3r_1d^3r_2 = E \int \int \phi_{1s}(r_1)\phi_{1s}(r_2)\phi_{1s}(r_2)\phi_{nL}(r_3)d^3r_1d^3r_2 \]  

(7)

or

\[ \left(-\frac{1}{2} \nabla^2 r_3 - \frac{3}{r_3} + 2 \int \frac{\phi_{1s}^2(r)}{|r_3 - r|} dr\right) \phi_{nL}(r_3) = E^1 \phi_{nL}(r_3), \]  

(8)

where \( E = E^0 + E^1 \) and Equation (8) is the Schrodinger equation for the valence electron; consequently, the effective potential for the valence electron is shown in Equation (9).

\[ V(r) = -\frac{3}{r} + 2 \int \frac{\phi_{1s}^2(r')}{|r - r'|} dr', \]  

(9)

where we have made the changes \( r_3 = r \) and \( r = r' \). The form of the \( \phi_{1s} \) wave function is given by [2], Equation (10).

\[ \phi_{1s}(r) = \frac{1}{\sqrt{\pi}} (a)^{3/2} e^{-ar} \]  

(10)

In Equation (10), \( a = 2.6875 \) and it is calculate through variational methods [2]. If the Equation (10) is inserted in Equation (9), the final form of the effective potential can be found, and it is shown in Equation (11).

\[ V(r) = -\frac{3}{r} + \frac{2}{r} \left[ 1 - (1 + ar)e^{-2ar} \right] \]  

(11)

In addition, the relationship between the reduced potential \( U(r) \) in Equation (1) and the effective potential \( V \) given in Equation (11) is given by \( U(r) = 2mV(r)/\hbar^2 \). At this point, we can solve Equation (1) and use Equation (11) in order to calculate the bound states energies \( E^1 \) that correspond to \( \hat{H}^1 \) by means of \( E^1 = k^2/2 \). Finally, the ground state energy is found with \( E = E^0 + E^1 = -7.279913387 + \frac{k^2}{2} \).
4. Results and discussion
The Hankel functions are complex functions, hence the solutions of Equation (1) are complex functions too, but it is known that the solution of Equation (1) must be real when the \( k \) wave number satisfies \( \text{Re}(k) = 0 \) [7]. Figure 1(a) shows an arbitrary solution of Equation (1), where the potential given by Equation (11) and the arbitrary values \( k = 5i \) and \( L = 0 \) have been used. The following aspects are observed: first, the function is real; second, when the \( r \) distance tends to infinity, the \( F_L(k = 5i, r) \) function tends to be constant, which is the behavior predicted by the Equation (2), and, in this way we have calculated the Jost function \( f_{L=0}(k = 5i) \). We repeat this process in order to find the \( k \) value that satisfies both relations \( \text{Im}(k) > 0 \) and \( \text{Re}(k) = 0 \), and for which \( f_L(k) = 0 \).

![Figure 1](image)

Figure 1. (a) Solution of Equation (1) for \( k = 5i \) and \( L = 0 \), (b) Jost function as a function of the \( k \) wave number, \( \text{Re}(k) = 0 \), for \( k = 0.5917i \), \( f_0(k) = 0 \).

| State        | \( E^a (eV) \) | \( E^b (eV) \) | \( E^c (eV) \) | \( E_{\text{exp}} (eV) \) |
|--------------|----------------|----------------|----------------|----------------|
| Ground state | -192.0         | -201.2         | -202.8         | -203.5         |
| Error (%)    | 5.7            | 1.1            | 0.3            | -              |

\( a \) Perturbation method until first order [2].
\( b \) Variational method [2].
\( c \) This work.

In Table 1 the ground state energy of lithium atom, which was calculated with different simple methods of approximations, is shown. These graphics were obtained using three different initial conditions in Equation (1); it is seen that the \( k \) value for which \( f_L(k) = 0 \) does not dependent on the initial conditions [16]. As for \( k = 0.5917i \), \( f_0(k) = 0 \), with this value we can calculate the energy \( E^1 \). Note that in Figure 1(b) only the point \( k = 0.5917i \) has physical interpretation.

In Table 4 the ground state energy of lithium atom, which was calculated with different simple methods of approximations, is shown. In this work, an error of 0.3% with respect to the experimental value was obtained; although the method proposed here is very simple, it produces better results than others more complex methods such as the perturbation method and the variational method which report errors of 5.7% and 1.1%, respectively. As a result, we have proposed a method which is easy to implement, and it could be extended to work with atoms with more electrons.
5. Conclusions

The lithium atom was modeled in a simple way as a collision of one electron with an ionized lithium atom. It was possible because we considered the Hamiltonian of lithium atom as the joint of two Hamiltonian, i.e, $H = H^0 + H^1$, where $H^0$ represents an ionized lithium atom and $H^1$ was interpreted as a collision of one electron with a nucleus (of Z=3) and two 1s electrons; therefore, we used the Scattering Theory to calculated the ground state energy of $H^1$. Finally we found the electronic energy as the sum of energies that correspond to $H^0$ and $H^1$. The results that have been found match those of the experimental values.

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