

# Lithium red, crude approximation.

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## Abstract

Burning Lithium produces a vivid red flame, with peak emission roughly around  $670 \pm 10$  nm. The objective of this problem is to solve the Lithium atom for the red transition under a crude approximation.

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# 1 Introduction

In the case of an hydrogenoid system the Hamiltonian can be represented analyzing the structure of the atom as a two body problem, consisting in a light attractor and an heavy core. It is therefore ideal to move to the Center-of-Mass and Relative coordinates, after which is possible to express the complete Hamiltonian, notice that for these analysis the Center-of-Mass Hamiltonian is ignored since we are mainly interested on the relativistic motion of the electrons on the shells.

$$H = \frac{|\vec{p}|^2}{2\tilde{m}} + V(|\vec{r}|) \quad (1)$$

Where  $\vec{p}$  is the Relative momentum,  $\tilde{m}$  is the reduced mass. In order to express the wavefunctions in real space we rewrite the momentum using the laplacian in spherical coordinates  $(r, \theta, \varphi)$  and the orbital angular momentum  $\vec{L}$ .

$$H = -\frac{\hbar^2}{2m} \frac{1}{r^2} \frac{\partial}{\partial r} r^2 \frac{\partial}{\partial r} + \frac{L^2}{2mr^2} + V(|\vec{r}|) \quad (2)$$

$H$  can be decomposed in its radial and angular parts and hence the eigenfunctions  $\psi(r, \theta, \varphi)$  can be written as

$$\psi(r, \theta, \varphi) = R_{n,l}(r) Y_{l,m}(\theta, \varphi) \quad (3)$$

where we introduce the quantum numbers  $(n, l, m)$ , that can be seen as labels referring to specific quantum states. The quantum numbers follow specific rules that define the allowed states of an electron in an atom:

- Principal Quantum Number ( $n$ ): This quantum number determines the energy level and size of the orbital, in particular we have  $n \in \mathbb{N}$
- Azimuthal (Orbital) Quantum Number ( $l$ ): Is dependent on the values of  $n$ , in particular we have:  $l \in [0, n - 1]$ . The values of  $l$  are commonly adressed using letters

Orbital Type	s	p	d	f	g	h
$l$	0	1	2	3	4	5

- Magnetic Quantum Number ( $m$ ): It depends on  $l$  and has integer values,  $m \in [-l, l]$

## 2 Solution

### 2.1 Wavefunctions and Energies

To list and write, in real-space spherical coordinates, the wavefunctions of the electrons, starting from the orbitals, we first need to express the Radial part of the wavefunction and the Angular part as functions of the quantum numbers. The angular part  $Y_{l,m}(\theta, \varphi)$  is described by spherical harmonics, which are a well known solution. The radial wavefunction for a hydrogen-like atom is instead obtained by solving the Schrödinger equation  $H\psi = E\psi$  which for the radial part

expressed as  $R(r) = \frac{P(r)}{r}$  reads:

$$\left( -\frac{\hbar}{2m} \frac{\partial^2}{\partial r^2} + \frac{\hbar l(l+1)}{2mr^2} - \frac{Z_{eff}e^2}{4\pi\epsilon_0 r} \right) P(r) = EP(r) \quad (4)$$

By solving this equation using the Laguerre Polynomials,  $L_{n-l-1}^{2l+1}$  we obtain the final expression

$$R_{n,l}(r) = N_{n,l} \left( \frac{2Z_{eff}r}{na_0} \right)^l e^{-Z_{eff}r/na_0} L_{n-l-1}^{2l+1} \left( \frac{Z_{eff}r}{na_0} \right) \quad (5)$$

where  $N_{n,l} = \sqrt{\left( \frac{2Z_{eff}}{na_0} \right)^3 \frac{(n-l-1)!}{2n(n+1)!}}$  is the normalization constant.

From this result we also obtain the eigenvalue of the Hamiltonian, which corresponds to the Energy levels, notice how the energy values depends only on the quantum number n.

$$E_{n,l} = -\frac{m_e e^4 Z_{eff}^2}{8\epsilon_0 \hbar} \frac{1}{n^2} \quad (6)$$

- $|1s\rangle$ : n=1, l=0, m=0.

$$\begin{aligned} Y_{0,0} &= \sqrt{\frac{1}{4\pi}} \\ R_{1,0}(r) &= 2\sqrt{\left( \frac{Z_{eff}}{a_0} \right)^3} e^{-Z_{eff}r/a_0} \\ E_{1s} &= -122.4 \text{ eV} \end{aligned}$$

- $|2s\rangle$ : n=2, l=0, m=0.

$$\begin{aligned} Y_{0,0} &= \sqrt{\frac{1}{4\pi}} \\ R_{2,0}(r) &= \frac{1}{\sqrt{2}} \sqrt{\left( \frac{Z_{eff}}{a_0} \right)^3} e^{-Z_{eff}r/2a_0} \left( 1 - \frac{Z_{eff}r}{2a_0} \right) \\ E_{2s} &= -30.6 \text{ eV} \end{aligned}$$

- $|2p\rangle$ :

– n=2, l=1, m=0.

$$\begin{aligned} Y_{1,0} &= \sqrt{\frac{3}{4\pi}} \sin(\theta) \\ R_{2,1}(r) &= \frac{1}{2\sqrt{6}} \sqrt{\left( \frac{Z_{eff}}{a_0} \right)^3} e^{-Z_{eff}r/2a_0} \left( \frac{Z_{eff}r}{a_0} \right) \\ E_{2p} &= -30.6 \text{ eV} \end{aligned}$$

–  $n=2, l=1, m=\pm 1$ .

$$Y_{1,\pm 1} = \mp \sqrt{\frac{3}{8\pi}} \sin(\theta) e^{\pm i\varphi}$$

$$R_{2,1}(r) = \frac{1}{2\sqrt{6}} \sqrt{\left(\frac{Z_{eff}}{a_0}\right)^3} e^{-Z_{eff}r/2a_0} \left(\frac{Z_{eff}r}{a_0}\right)$$

$$E_{2p} = -30.6 \text{ eV}$$

Where we have  $Z_{eff} = 3$  since we are in the case of the Lithium atom.

As expected the energy is the same for orbitals having the same principal number.

## 2.2 Charge Density

The charge density  $\rho$  is given by the probability density of finding a particle at position  $\vec{r}$ :  $|\psi_i(r)|^2$ , multiplied by the charge of the corresponding particle. In the given case, the charge density for the two electrons in the 1s state is:

$$\rho(r) = -2e \cdot |\psi_{1s}(r)|^2 \quad (7)$$

The wavefunction is the one previously obtained

$$\psi_{1s} = 2\sqrt{\frac{1}{4\pi} \left(\frac{3}{a_0}\right)^3} e^{-3r/a_0} \quad (8)$$

In conclusion we have

$$\begin{aligned} \rho(r) &= -2e \left( 2\sqrt{\frac{1}{4\pi} \left(\frac{3}{a_0}\right)^3} e^{-3r/a_0} \right)^2 \\ &= -e \frac{54}{\pi a_0^3} e^{-6r/a_0} \end{aligned} \quad (9)$$

## 2.3 Electrostatic Potential

Gauss law is one of the Maxwell equation, it describes how the electric flux through a confined area is related to the charges enclosed within that surface.

$$\oint_{\partial V} \mathbf{E} \cdot d\mathbf{A} = \frac{Q_{enc}}{\epsilon_0} \quad (10)$$

Since the electric field is the gradient of the electrostatic potential is possible to obtain the potential starting from the Gauss's law. Expressing the electric charge as the spatial integral of the charge

density, we obtain the Poisson's equation

$$\nabla^2 \Phi(r) = -\frac{\rho(r)}{\epsilon_0}$$

Even though this formulation is more straightforward, in the following we will directly apply the Gauss's law, obtaining firstly the enclosed charge and secondly the electrostatic potential; this approach gives a deeper understanding of the physics behind the process.

We begin computing the charge enclosed,  $Q_{enc}$  within a volume of radius  $r$ .

$$\begin{aligned} Q_{enc} &= \int_0^r 4\pi r'^2 \rho(r') dr \\ &= e \left( \left( 1 + \frac{6r}{a_0} + \frac{18r^2}{a_0^2} \right) e^{-6r/a_0} - 1 \right) \end{aligned} \quad (11)$$

Ultimately we obtain the electrostatic potential by integrating the electric field, following the general electrostatic approach

$$\Phi = - \int_{+\infty}^r \frac{1}{4\pi r \epsilon_0} Q_{enc} \quad (12)$$

From which we obtain the formulation

$$\Phi(r) = \frac{e}{4\pi r \epsilon_0} (a_0 e^{-6r/a_0} (a_0 + 3r) - 1)$$

## 2.4 Perturbation theory

In the following we consider the electrostatic potential of the previous section as a perturbative Hamiltonian  $H_{per} = -e\Phi(r)$ . This formulation allows us to find corrections to the atomic energy levels using perturbation theory, exploiting the shell structure of atomic orbitals. The expected result from this approach is to detect a stronger total energy for the electron further from the core, therefore a more pronounced positive energy shift.

In order to simplify the calculations we translate the expression of the electrostatic potential and the wavefunctions in atomic units, the new formulation for the potential is

$$\Phi(r) = \frac{1}{r} (e^{-2rZ} (1 + Zr) - 1)$$

In the following formulation we will use first order degenerative perturbation theory. In order to calculate the energy correction derived by a potential  $\Phi(r)$  it is sufficient to calculate the projectors  $\Pi_{\epsilon_n^{(0)}}$  over the eigenstates having degenerate energy eigenvalue. We can imagine to have three main vectors acting on the matrix of the Hamiltonian:  $|1s\rangle$ ,  $|2s\rangle$ ,  $|2p\rangle$ ; we have that the projector onto

the eigenvectors having degenerate eigenvalues is

$$\Pi_{\epsilon_1^{(0)}} = \begin{bmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{bmatrix}$$

Starting from this analysis is possible to derive the first order perturbed Hamiltonian,

$$H_{eff}^1 = \Pi_{\epsilon_1^{(0)}} (-e \cdot \Phi(r)) \Pi_{\epsilon_1^{(0)}} \quad (13)$$

Whose solution is a  $2 \times 2$  matrix whose final expression is the following

$$H_{eff}^1 = \begin{bmatrix} \langle 2s|V|2s \rangle & \langle 2s|V|2p \rangle \\ \langle 2p|V|2s \rangle & \langle 2p|V|2p \rangle \end{bmatrix} \quad (14)$$

In this case the off diagonal terms turns out to be zero and we obtain as a result for the first order energy correction to the states  $|2s\rangle$ ,  $|2p\rangle$ :

$$E_{2s}^{(1)} = 17.13 \text{ eV}$$

$$E_{2p}^{(1)} = 19.82 \text{ eV}$$

We have obtained a fundamental result in the description of the energies of the orbitals of an atom, more precisely the degeneration for states having the same principal quantum number is removed. As expected the energy shifting is more pronounced for the  $|2p\rangle$  orbital, whose electrons ends up having an energy closer to the ionization energy.

## 2.5 Red Lithium flame frequency

It is now possible to compare the results obtained for the difference in energies to the wavelength of the red flame of the lithium atom. More precisely this wavelength emission derives from the electrons that after being excited to the higher energy level, due to the combustion, eventually returns to the original orbital emitting a photon of energy

$$\Delta E = E_{2p} - E_{2s} \quad (15)$$

This energy is directly related to the wavelength of the photon by means of the planck constant and the speed of light, in particular we have

$$\lambda = \frac{c}{\nu} = \frac{c \hbar}{\Delta E}$$

We proceed therefore to measure this value from the results previously obtained for the energy of the states  $|2s\rangle$ ,  $|2p\rangle$ . Starting from an energy difference of  $\Delta E = 2.6 \text{ eV}$  we obtain as a final



result.

$$\lambda = 461 \text{ nm} \quad (16)$$

At first glance this result is disappointing compared to the expected value of 670 nm, nonetheless is still a significant result. That's because what obtained is simply a first order correction that can be significantly improved by utilizing second order perturbation theory.

## 2.6 Second Order Perturbation theory

The formulation for the correction at the second order for the perturbed Hamiltonian is:

$$H_{eff}^2 = \Pi_{\epsilon_1^{(0)}} H_{Per} R_{\epsilon_1^{(0)}} H_{Per} \Pi_{\epsilon_1^{(0)}} \quad (17)$$

Where we introduced as  $R_0$  the "Moore Penrose Pseudoinverse",  $R_{\epsilon_1^{(0)}} = (\mathbb{I} \cdot \epsilon_1 - H_0)^{-1}$  for the degenerate eigenvalues of the states  $|2s\rangle$ ,  $|2p\rangle$ . From this equation we derive the following solution

$$H_{eff}^2 = \frac{1}{\epsilon_{1s}} \begin{bmatrix} \langle 2s | H_{Per} | 1s \rangle & \langle 1s | H_{Per} | 2s \rangle & \langle 2p | H_{Per} | 1s \rangle & \langle 1s | H_{Per} | 2p \rangle \\ \langle 2s | H_{Per} | 1s \rangle & \langle 1s | H_{Per} | 2p \rangle & \langle 2p | H_{Per} | 1s \rangle & \langle 1s | H_{Per} | 2p \rangle \end{bmatrix} \quad (18)$$

As in the first order perturbation theory the off diagonal terms ends up being zero, therefore, we find that the second order corrections for the 2s, 2p states is

$$E_{2s}^{(2)} = 0.44 \text{ eV}$$

$$E_{2p}^{(2)} = 0.00 \text{ eV}$$

The results looks convincing, in particular we have that the energy difference between the two levels is decreased, hence the value of the wavelength will increase and be closer to the expected result. The null energy correction for the  $|2p\rangle$  could be explained by the non presence of perturbation coming from the intermediate  $|1s\rangle$  state. We proceed to calculate the new wavelength given the new energy difference:

$$\Delta E = 2.25 \text{ eV} \quad (19)$$

and therefore the obtained result for the emitted wavelength is

$$\lambda = 551 \text{ nm} \quad (20)$$

As we can see the previous result has significantly improved, even tough the value obtained is not precisely what expected we understood that by considering more level of perturbation we could get even a more precise result.





### 3 Conclusion

In this report, we solved the Lithium atom for the red transition at the crudest approximation, in particular we have successfully described the wavefunctions of the principal orbitals reachable by the Lithium atom electrons and the corresponding energies. Using perturbation theory, considering the Electrostatic potential as a perturbative Hamiltonian it was possible to remove the energy level degeneracy of orbitals having the same principal quantum number. This energy separation allowed to perform a new analysis not available before, and determine an approximation of the energy of the photon generated by emission after the de-excitement of an electron from  $|2p\rangle$  to state  $|2s\rangle$ .

Another aspect to analyze while considering the energy-level degeneracy is the fact that the perturbation theory didn't manage to remove all degeneracy. As a matter of fact, states of the orbital  $|2p\rangle$ , having the same magnetic quantum number  $m$  ended up having the same energy shift. To remove all the energy-level degeneracy we should implement other physical properties such as the Spin orbit coupling and the Zeeman effect.