



UNIVERSITÀ  
DEGLI STUDI  
DI PADOVA

Dipartimento di Fisica  
e Astronomia  
Galileo Galilei



# Assignment 2

## Lithium red crude approximation

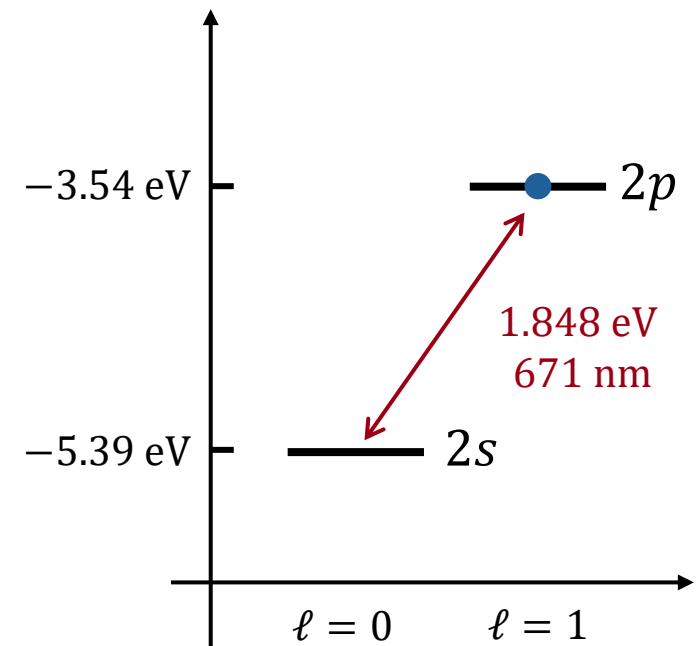
Quantum Information with  
Atoms and Photons

PROF. PIETRO SILVI

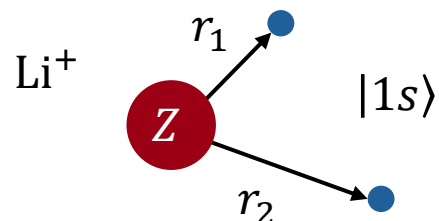
PROF. MARCO FEDELE DI LIBERTO

ALESSANDRO MIOTTO

Burning lithium produces a vivid **red flame** due to photon emission from **electron transitions between the  $2s$  and  $2p$  states**, corresponding to a wavelength of  $670.9\text{ nm}$



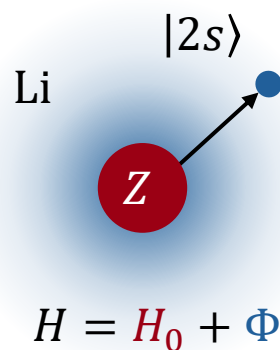
# Strategy



We first occupy the state  $|1s\rangle$  with **two electron**, treating the ion  $\text{Li}^+$  as an helium-like atom

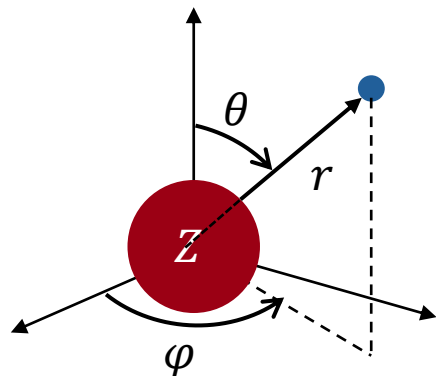
Then we compute the **potential  $\Phi$**  induced by the electrons **charge density  $\rho$**

Diagram showing a  $\text{Li}^+$  ion (red circle with  $Z$ ) surrounded by a blue charge density cloud. The Poisson equation is given as  $\nabla^2 \Phi = -4\pi\rho$  and the potential as  $V = -\frac{Z}{r}$ .



This give a **perturbative term** in the hamiltonian of the **third electron**  $|2s\rangle$  and  $|2p\rangle$

# Radial Schrödinger Equation



**hydrogen-like hamiltonian**

$$\left(-\frac{1}{2}\nabla^2 - \frac{Z}{r}\right)\psi(\mathbf{r}) = E\psi(\mathbf{r})$$

separation of variables

$$\psi(\mathbf{r}) = R_{n\ell}(r)Y_{\ell}^m(\theta, \varphi)$$

$$u(r) := rR(r)$$

**Spherical harmonics**,  
eigenfunctions of the  
angular momentum  $L$ .  
Depends on the quantum  
numbers  $\ell, m$

$$\left(-\frac{1}{2}\frac{d^2}{dr^2} - \frac{Z}{r} + \frac{\ell(\ell+1)}{2r^2}\right)u(r) = Eu(r)$$

$$E_n = -\frac{Z^2}{2n^2}$$

$n = 1$

$$\psi_{1s}(\mathbf{r}) = \frac{Z^{3/2}}{\sqrt{\pi}}e^{-Zr}$$

$$E_{1s} = -\frac{Z^2}{2}$$

$n = 2$

$$\psi_{2s}(\mathbf{r}) = \frac{Z^{3/2}}{\sqrt{32\pi}}(2 - Zr)e^{-\frac{Zr}{2}}$$

$$\psi_{2p}(\mathbf{r}) = \frac{Z^{3/2}}{\sqrt{32\pi}}Zre^{-\frac{Zr}{2}}\cos\theta$$

$$E_{2s} = E_{2p} = -\frac{Z^2}{8}$$

$|2s\rangle$  and  $|2p\rangle$  are degenerate, therefore the  
transition  $|2s\rangle \rightarrow |2p\rangle$  does not exhibit  
spectral emission

Atomic units:  $\hbar = m = 4\pi\epsilon_0 = a_0 = 1$ . Energy is  
expressed in **Hartree**  $1 \text{ Ha} = 27.22 \text{ eV}$ .

# $|1s\rangle$ electrons - $\text{Li}^+$

As wavefunction we use the product of the two  $|1s\rangle$  states

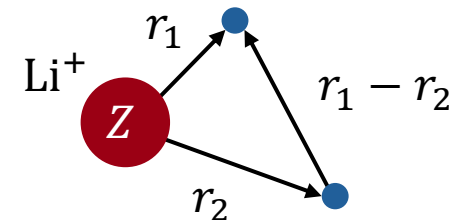
$$\psi(\mathbf{r}) = \psi_{1s}(\mathbf{r})\psi_{1s}(\mathbf{r}) = \frac{Z^3}{\pi} e^{-2Zr}$$

As hamiltonian we have the sum of **two single electron** hamiltonian

The **Coulomb repulsion** is the **perturbative** term

$$H = \underbrace{\underbrace{-\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1}}_{\text{first electron hamiltonian}} + \underbrace{-\frac{1}{2}\nabla_2^2 - \frac{Z}{r_2}}_{\text{second electron hamiltonian}}}_{H_0} + \underbrace{\frac{1}{|\mathbf{r}_1 - \mathbf{r}_2|}}_V$$

Coulomb interaction

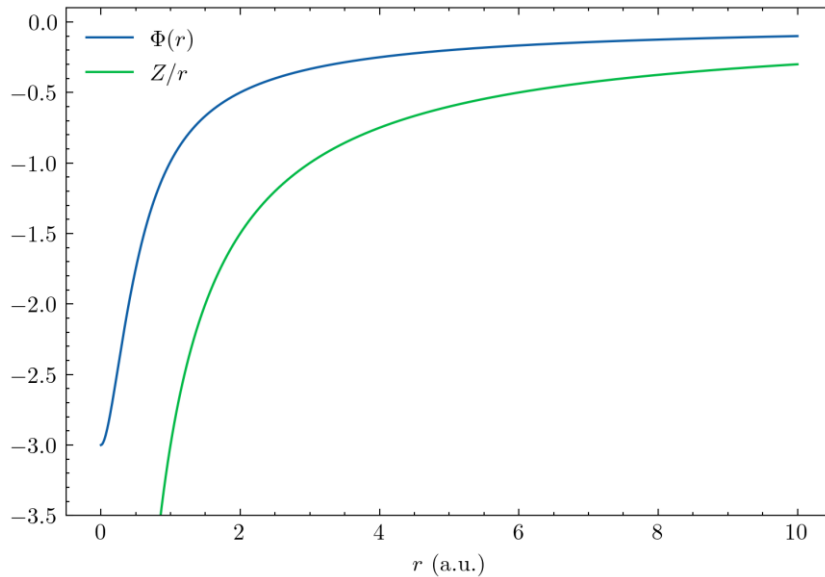


$$\left. \begin{aligned} E^{(0)} &= \langle 1s | H_0 | 1s \rangle = 2 \left( -\frac{Z^2}{2} \right) = -9 \text{ Ha} = -244 \text{ eV} \\ \Delta E^{(1)} &= \langle 1s | V | 1s \rangle = \int d^3\mathbf{r}_1 d^3\mathbf{r}_2 \frac{|\psi(\mathbf{r})|^2}{|\mathbf{r}_1 - \mathbf{r}_2|} = \frac{5}{8} Z = 51 \text{ eV} \end{aligned} \right\} \begin{aligned} E^{(1)} &= -193 \text{ eV} \\ 2.5\% \text{ error} \\ E_{\text{exp}} &= -198 \text{ eV} = \\ &= -(I_2 + I_3) \end{aligned}$$

# $|1s\rangle$ electrons – charge density potential

We want to find the **potential**  $\Phi$  produced by the electrons in  $|1s\rangle$ . This is the **perturbation** experienced by the electron in the second orbital

$$H = H_0 + \Phi$$



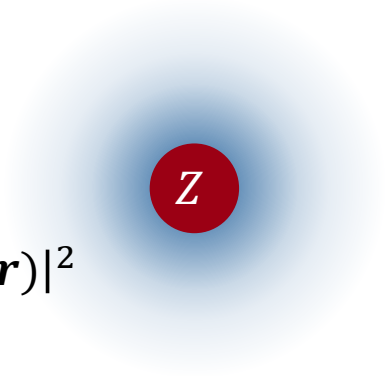
Charge Density

$$\rho(\mathbf{r}) = -\sum_i |\psi_i(\mathbf{r})|^2 = -2|\psi_{1s}(\mathbf{r})|^2$$

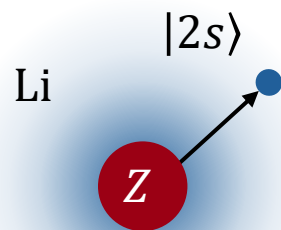
$$\nabla^2 \Phi = -4\pi\rho$$

To find the potential we use the **Poisson equation's** Green function

$$\Phi(\mathbf{r}) = \int d^3\mathbf{r}' \frac{\rho(\mathbf{r}')}{|\mathbf{r}' - \mathbf{r}|} = \frac{1}{r} [(Zr + 1)e^{-2Zr} - 1]$$



# $|2s\rangle$ and $|2p\rangle$ electron: first-order perturbation



$$H = H_0 + \Phi$$

$$H = \overbrace{-\frac{1}{2}\nabla^2 - \frac{Z}{r}}^{\text{third electron hamiltonian}} + \Phi = H_0 + \Phi$$

The **potential  $\Phi$**  generated by the **two electrons** in  $|1s\rangle$  can be treated as a perturbation

$n = 2$

$$\psi_{2s}(\mathbf{r}) = \frac{Z^{3/2}}{\sqrt{32\pi}} (2 - Zr) e^{-\frac{Zr}{2}}$$

$$\psi_{2p}(\mathbf{r}) = \frac{Z^{3/2}}{\sqrt{32\pi}} Zr e^{-\frac{Zr}{2}} \cos \theta$$

$$E_{2s} = E_{2p} = -\frac{Z^2}{8}$$

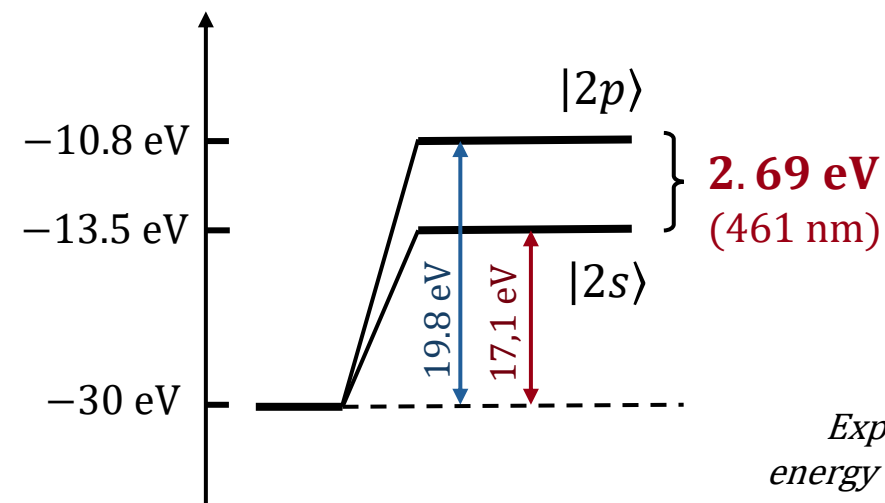
*Zero-Order energy*

$$E_{2s,2p}^{(0)} = \langle 2s | H_0 | 2s \rangle = \langle 2p | H_0 | 2p \rangle = -\frac{Z^2}{8} = -30 \text{ eV}$$

*First-Order corrections*

$$\Delta E_{2s}^{(1)} = \langle 2s | \Phi | 2s \rangle = \int d^3\mathbf{r} |\psi_{2s}(\mathbf{r})|^2 \Phi(\mathbf{r}) = \frac{17}{81} Z = 17.1 \text{ eV}$$

$$\Delta E_{2p}^{(1)} = \langle 2p | \Phi | 2p \rangle = \int d^3\mathbf{r} |\psi_{2p}(\mathbf{r})|^2 \Phi(\mathbf{r}) = \frac{59}{243} Z = 19.8 \text{ eV}$$



*Experimental  
energy transition  
1.848 eV  
(671 nm)*

# $|2s\rangle$ and $|2p\rangle$ electron: degenerate perturbation theory

Given the degeneracy of the second orbital, we have  
to use the **degenerate perturbation theory**

$$H = H_0 + V$$

$$H_0 = E_{1s}|1s\rangle\langle 1s| + E_{2s,2p}(|2s\rangle\langle 2s| + |2p\rangle\langle 2p|) = -\frac{Z^2}{8} \begin{pmatrix} 4 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

$$V = \begin{pmatrix} \langle 1s|\Phi|1s\rangle & \langle 1s|\Phi|2s\rangle & \langle 1s|\Phi|2p\rangle \\ \langle 2s|\Phi|1s\rangle & \langle 2s|\Phi|2s\rangle & \langle 2s|\Phi|2p\rangle \\ \langle 2p|\Phi|1s\rangle & \langle 2p|\Phi|2s\rangle & \langle 2p|\Phi|2p\rangle \end{pmatrix}$$

$$\Pi = |2s\rangle\langle 2s| + |2p\rangle\langle 2p| = \begin{pmatrix} 0 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{pmatrix}$$

*Projection on the  
degenerate eigenspace*

$$R = (E_{2s,2p}\Pi - H_0)^{-1} = \frac{8}{3Z^2} \begin{pmatrix} 1 & 0 & 0 \\ 0 & 0 & 0 \\ 0 & 0 & 0 \end{pmatrix}$$

*Moore-Penrose  
pseudoinverse*

As orthonormal basis, we choose the  
hydrogen-like wavefunctions

$$|1s\rangle = \begin{pmatrix} 1 \\ 0 \\ 0 \end{pmatrix} \quad |2s\rangle = \begin{pmatrix} 0 \\ 1 \\ 0 \end{pmatrix} \quad |2p\rangle = \begin{pmatrix} 0 \\ 0 \\ 1 \end{pmatrix}$$

$$E_{1s} = -\frac{Z^2}{2} \quad E_{2s,2p} = -\frac{Z^2}{8}$$



# $|2s\rangle$ and $|2p\rangle$ electron: second and third-order perturbation

**First-Order corrections**

$$H^{(1)} = \Pi V \Pi$$

(as before)

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

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

**Second-Order corrections**

$$H^{(2)} = \Pi V R V \Pi$$

$$\Delta E_{2s}^{(2)} = 0.579 \text{ eV}$$

$$\Delta E_{2p}^{(2)} = 0.0 \text{ eV}$$

**Third-Order corrections**

$$H^{(3)} = \Pi V R V R V \Pi - \Pi V \Pi V R^2 V \Pi$$

$$\Delta E_{2s}^{(3)} = 0.214 \text{ eV}$$

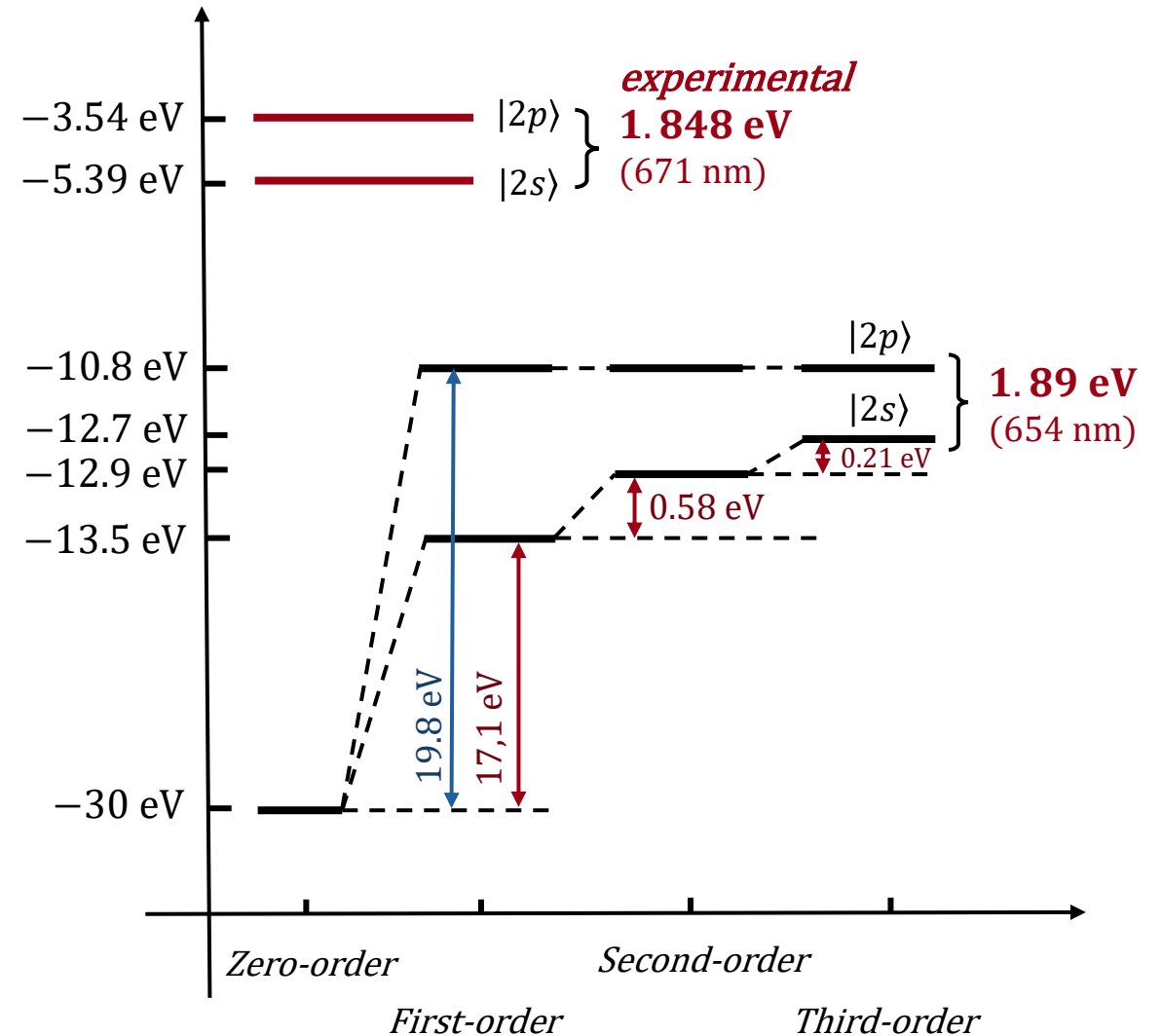
$$\Delta E_{2p}^{(3)} = 0.0 \text{ eV}$$

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$$E_{|2p\rangle \rightarrow |2s\rangle} = \Delta E_{2p} - \Delta E_{2s} = 1.894 \text{ eV}$$

(654 nm)

Experimental energy transition  
 1.848 eV (671 nm)  
 2.5% error



# One more thing: numerical approach

