Università degli Studi di Padova
Dipartimento di Fisica e Astronomia Galileo Galilei

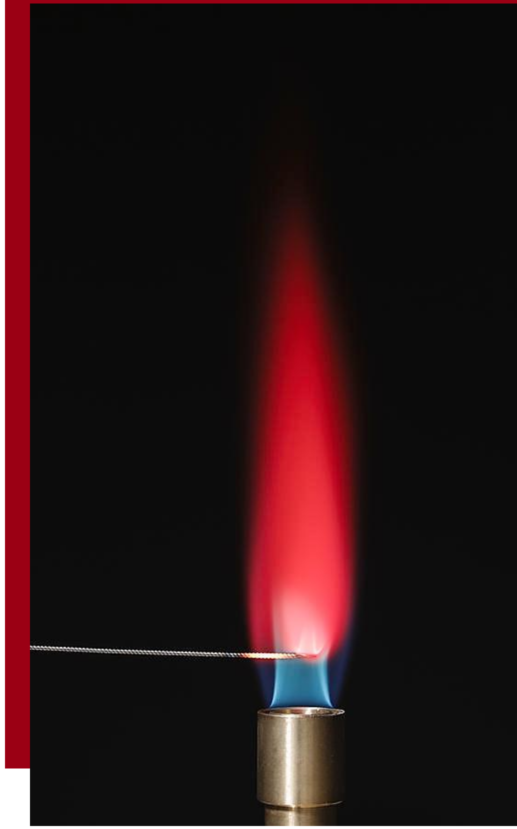
Assignment 2
Lithium red
crude approximation

Quantum Information with Atoms and Photons

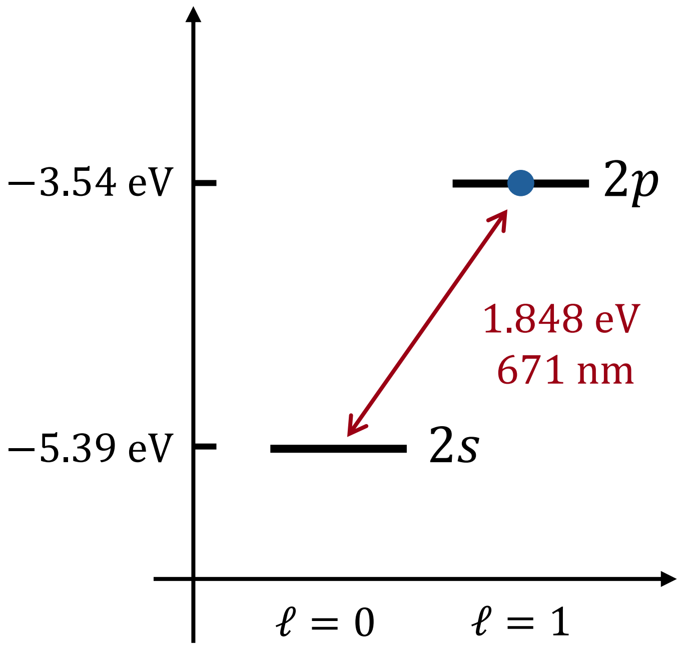
Prof. Pietro Silvi
Prof. Marco Fedele di Liberto

Alessandro Miotto

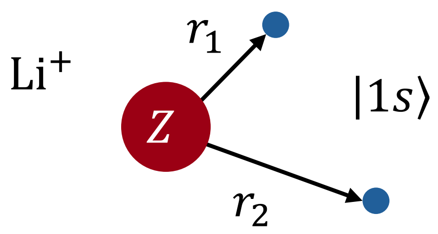
Introduction



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 nm

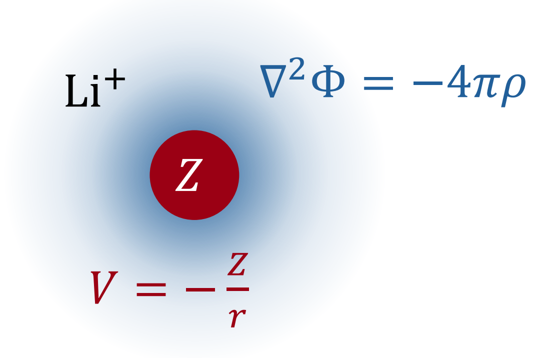


Strategy

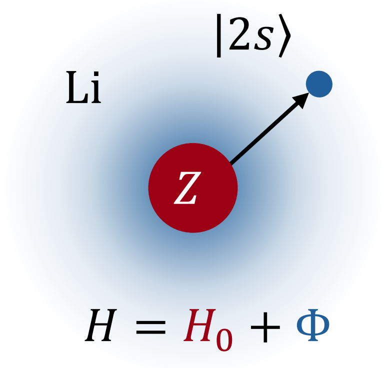


We first occupy the state $|1s\rangle$ with two electron, treating the ion Li^+ as an helium-like atom

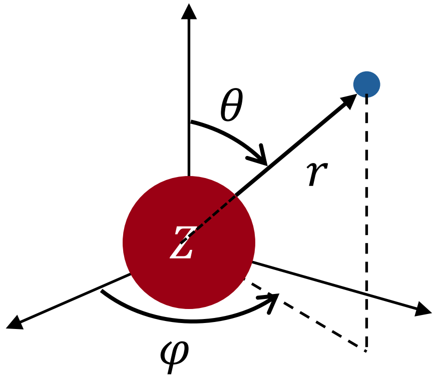
Then we compute the potential Φ induced by the electrons charge density ρ



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



Radial Schrödinger Equation



hydrogen-like hamiltonian

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

separation of variables

$$\psi(\boldsymbol{r}) = R_{n\ell}(r)\mathcal{Y}_\ell^m(\theta,\varphi)$$

$u(r) \coloneqq rR(r)$

Spherical harmonics, eigenfunctions of the angular momentum L. Depends on the quantum numbers ℓ, m

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

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

$n = 1$

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

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

$n = 2$

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

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

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

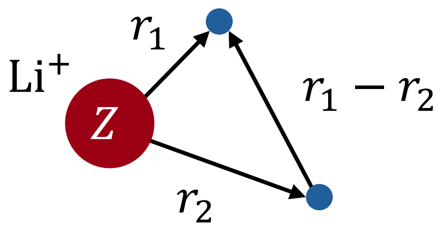
$|2s\rangle$ and $|2p\rangle$ are degenerate, therefore the transition $|2s\rangle \to |2p\rangle$ does not exhibit spectral emission

Atomic units: $\hbar = m = 4\pi\varepsilon_0 = a_0 = 1$. Energy is expressed in **Hartree** $1\ \mathrm{Ha} = 27.22\ \mathrm{eV}$.

$|1s\rangle$ electrons - Li^+

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

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



As hamiltonian we have the sum of two single electron hamiltonian

The Coulomb repulsion is the perturbative term

$$H = \underbrace{\underbrace{-\frac{1}{2}\nabla_1^2 - \frac{Z}{r_1}}_{\text{first electron hamiltonian}} \overbrace{-\frac{1}{2}\nabla_2^2 - \frac{Z}{r_2}}^{\text{second electron hamiltonian}}}_{H_0} + \underbrace{\underbrace{\frac{1}{|\boldsymbol{r_1} - \boldsymbol{r_2}|}}_{\text{Coulomb interaction}}}_{V}$$

$$E^{(0)} = \langle 1s|H_0|1s\rangle = 2\left(-\frac{Z^2}{2}\right) = -9\ \mathrm{Ha} = -244\ \mathrm{eV}$$

$$\Delta E^{(1)} = \langle 1s|V|1s\rangle = \int d^3\boldsymbol{r_1} d^3\boldsymbol{r_2} \frac{\psi(\boldsymbol{r})}{|\boldsymbol{r_1} - \boldsymbol{r_2}|} = \frac{5}{8}Z = 51\ \mathrm{eV}$$

$$\boldsymbol{E^{(1)} = -193\ \mathrm{eV}}$$

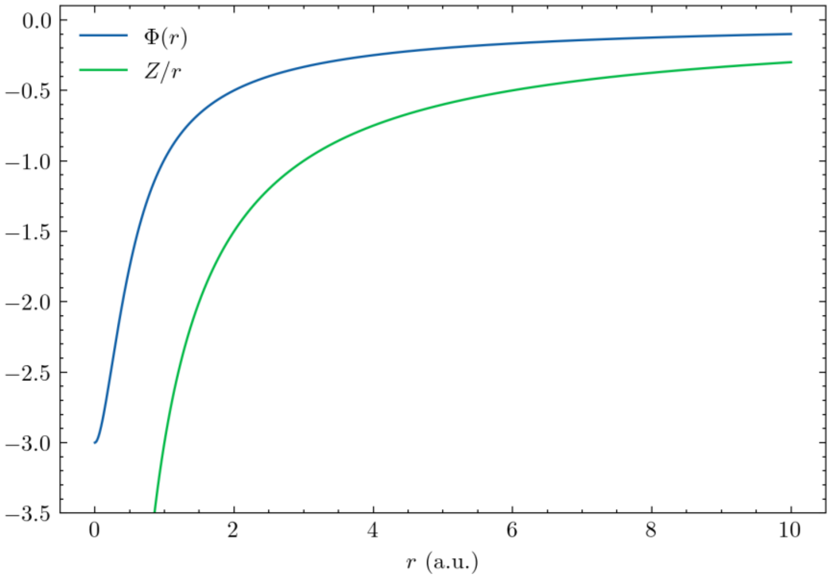
2.5% error

$$E_{exp} = -198\ \mathrm{eV} = -(\mathrm{I}_2 + \mathrm{I}_3)$$

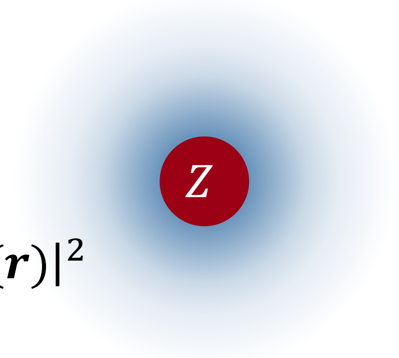
$|1s\rangle$ electrons – charge density potential

We want to find the **potential** Φ 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



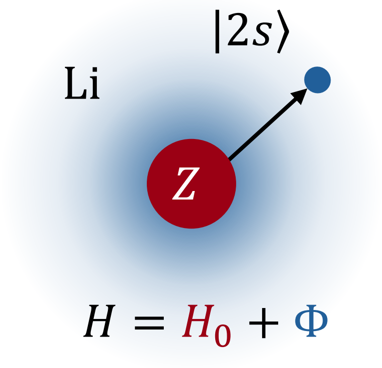
$$\rho(\boldsymbol{r}) = -\sum_i |\psi_i(\boldsymbol{r})|^2 = -2|\psi_{1s}(\boldsymbol{r})|^2$$

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

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

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

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



$$H = \underbrace{-\frac{1}{2}\nabla^2 - \frac{Z}{r}}_{\text{third electron hamiltonian}} + \Phi = \mathrm{H}_0 + \Phi$$

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

$n = 2$

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

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

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

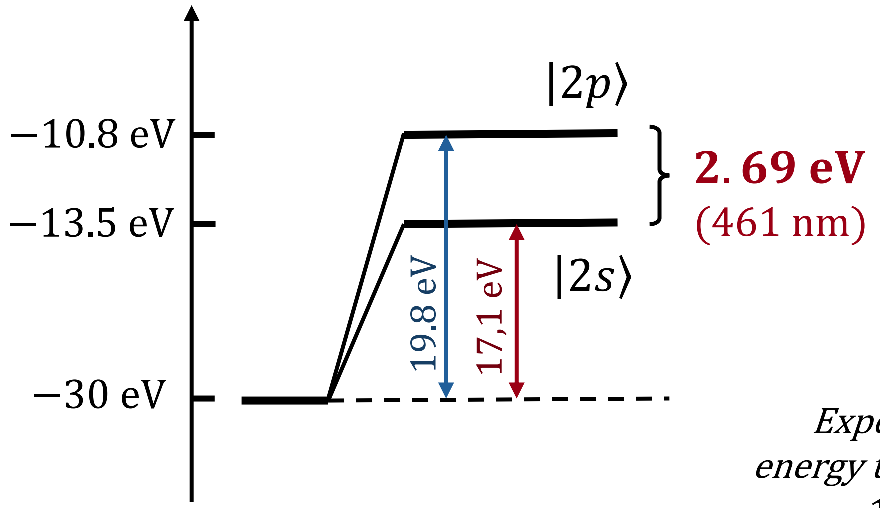
Zero-Order energy

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

First-Order corrections

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

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



Experimental energy transition
1.848 eV
(671 nm)

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

As orthonormal basis, we choose the hydrogen-like wavefunctions

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

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

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

$$H = H_0 + V$$

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

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

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

Projection on the degenerate eigenspace

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

Moore-Penrose pseudeinverse

$|2s\rangle$ 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

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

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

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

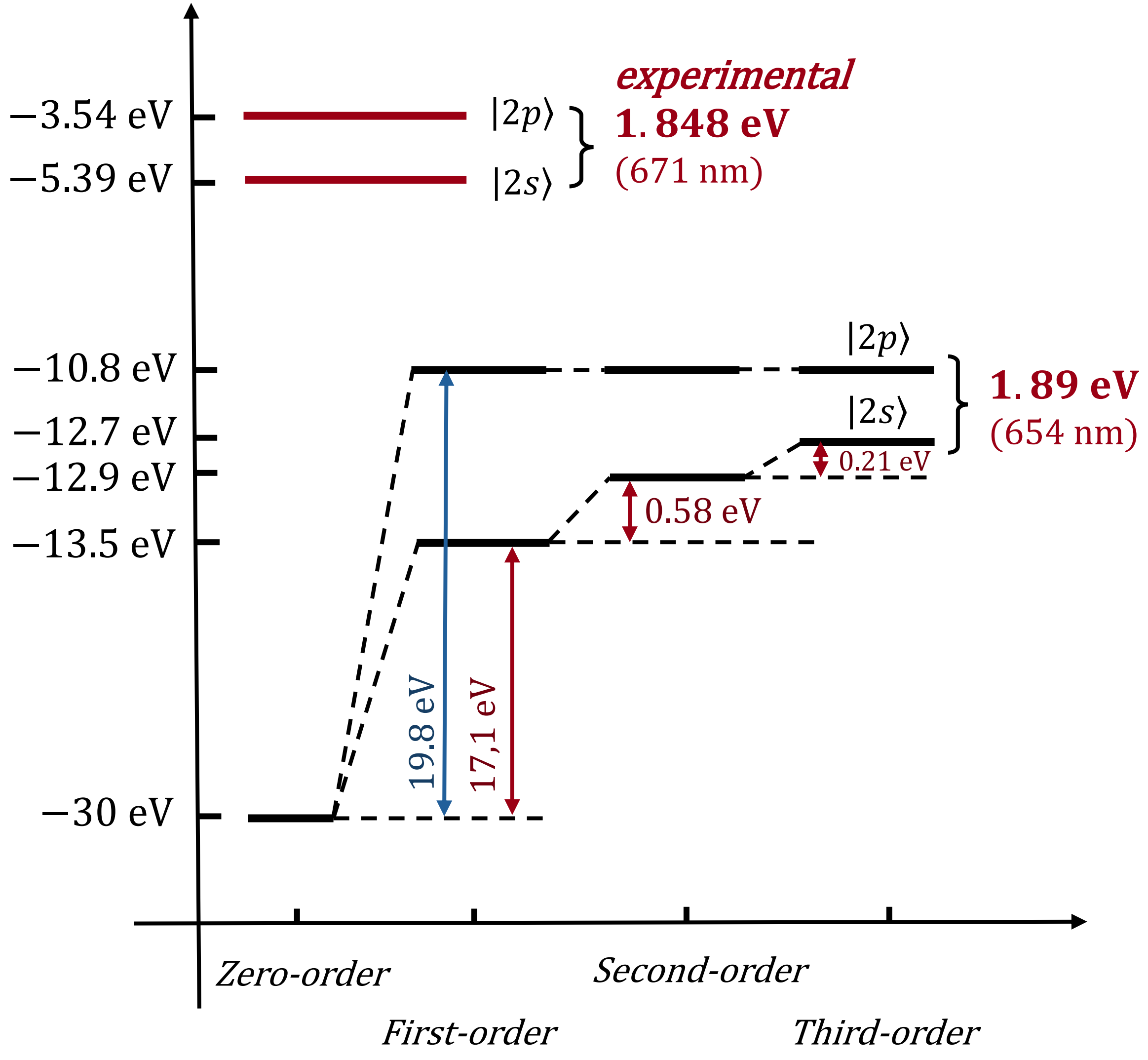
$$E_{|2p\rangle \to |2s\rangle} = \Delta E_{2p} - \Delta E_{2s} = 1.894 \text{ eV}$$

(654 nm)

Experimental energy transition

1.848 eV (671 nm)

2.5% *error*



One more thing: numerical approach

hydrogen-like wavefunctions as input

$$u_i^0(r)$$

charge density calculation

$$\rho^{(n)}(\boldsymbol{r}) = -\sum_j \left|\psi_j^{(n)}(\boldsymbol{r})\right|^2$$

resolution of the Poisson equation

$$\nabla^2\Phi^{(n)}(\boldsymbol{r}) = -4\pi\rho^{(n)}(\boldsymbol{r})$$

Shrödinger equation solver

$$\left[-\frac{1}{2}\frac{d^2}{dr^2} - \frac{Z}{r} + \Phi^{(n)} + \frac{\ell_i(\ell_i+1)}{2r^2}\right]u_i^{(n)}(r) = E_i^{(n)}u_i^{(n)}(r)$$

$$\{\psi_i(\boldsymbol{r}), E_i\}$$

repeat until convergence