PC3233 Assignment 4

May 14, 2024

1 Hydrogen Atom

Prove the identity for the Pauli matrices, $\boldsymbol{\sigma}$ and general vector operators $\mathbf{A}$ and $\mathbf{B}$:

$$(\boldsymbol{\sigma} \cdot \mathbf{A})(\boldsymbol{\sigma} \cdot \mathbf{B}) = (\mathbf{A} \cdot \mathbf{B}) + i\boldsymbol{\sigma} \cdot (\mathbf{A} \times \mathbf{B}) \tag{1}$$

1.1 Proof

$$(\boldsymbol{\sigma} \cdot \mathbf{A})(\boldsymbol{\sigma} \cdot \mathbf{B}) = \sum_{ij} \sigma_i A_i \sigma_j B_j \tag{2}$$

Since $\left[\sigma_i, \sigma_j\right] = \sigma_i\sigma_j - \sigma_j\sigma_i$, we can expand the above expression as:

$$\sum_{ij} \sigma_i A_i \sigma_j B_j = \sum_{ij} (\left[\sigma_i, \sigma_j\right] + \sigma_j\sigma_i) A_i B_j \tag{3}$$

Using the anticommutation property of the Pauli matrices, $\left\{\sigma_i, \sigma_j\right\} = \sigma_i\sigma_j + \sigma_j\sigma_i$ we have:

$$\begin{aligned}
\sum_{ij} (\left[\sigma_i, \sigma_j\right] + \sigma_j\sigma_i) A_i B_j &= \sum_{ij} (2i\epsilon_{ijk}\sigma_k A_i B_j + (\left\{\sigma_i, \sigma_j\right\} - \sigma_i\sigma_j) A_i B_j) \\
&= \sum_{ij} (2i\sigma_k (\mathbf{A} \times \mathbf{B})_k + 2\delta_{ij} A_i B_j - \sigma_i A_i \sigma_j B_j) \\
&= 2i\boldsymbol{\sigma} \cdot (\mathbf{A} \times \mathbf{B}) + 2\mathbf{A} \cdot \mathbf{B} - (\boldsymbol{\sigma} \cdot \mathbf{A})(\boldsymbol{\sigma} \cdot \mathbf{B})
\end{aligned}$$

Rearranging the terms, we have:

$$\begin{aligned}
(\boldsymbol{\sigma} \cdot \mathbf{A})(\boldsymbol{\sigma} \cdot \mathbf{B}) &= 2i\boldsymbol{\sigma} \cdot (\mathbf{A} \times \mathbf{B}) + 2\mathbf{A} \cdot \mathbf{B} - (\boldsymbol{\sigma} \cdot \mathbf{A})(\boldsymbol{\sigma} \cdot \mathbf{B}) \\
2(\boldsymbol{\sigma} \cdot \mathbf{A})(\boldsymbol{\sigma} \cdot \mathbf{B}) &= 2i\boldsymbol{\sigma} \cdot (\mathbf{A} \times \mathbf{B}) + 2\mathbf{A} \cdot \mathbf{B} \\
(\boldsymbol{\sigma} \cdot \mathbf{A})(\boldsymbol{\sigma} \cdot \mathbf{B}) &= (\mathbf{A} \cdot \mathbf{B}) + i\boldsymbol{\sigma} \cdot (\mathbf{A} \times \mathbf{B})
\end{aligned}$$

Hence, we have proved the identity.

2 Fine Structure

2.1 Determine the frequencies of absorption lines from 1S to 2P and 2P for (1H, 2D, 3T)

The reduced mass is given by:

$$\begin{cases} \mu_H = \frac{m_N m_e}{m_N + m_e} = 9.1044 \times 10^{-31} & \text{for Hydrogen, } m_N = m_p \\ \mu_D = \frac{m_N m_e}{m_N + m_e} = 9.1069 \times 10^{-31} & \text{for Deuterium, } m_N = m_p + m_n \\ \mu_T = \frac{m_N m_e}{m_N + m_e} = 9.1077 \times 10^{-31} & \text{for Tritium, } m_N = m_p + 2m_n \end{cases} \tag{4}$$

Then we can compute the energy levels of the hydrogen atom using the Bohr model, which is given by:

$$E_n = -\frac{\mu e^4 Z^2}{8\epsilon_0^2 h^2 n^2} \tag{5}$$

Therefore, we can get the energy difference between the 1S and 2P states by:

$$\Delta E_{1S-2P} = E_1 - E_2 \tag{6}$$

where E_1 and E_2 are the energy levels of the 1S and 2P states respectively.

$$\begin{cases} E_{1S-2P} = -2.178686 \times 10^{-18}\text{J} & \text{for Hydrogen} \\ E_{1S-2P} = -2.179279 \times 10^{-18}\text{J} & \text{for Deuterium} \\ E_{1S-2P} = -2.179477 \times 10^{-18}\text{J} & \text{for Tritium} \end{cases} \tag{7}$$

By using the Planck relation, $E = h\nu$, we can compute the frequency of the absorption lines:

$$\begin{cases} \nu_{1S-2P} = \frac{E_{1S-2P}}{h} = 2.466038 \times 10^{15}\text{Hz} & \text{for Hydrogen} \\ \nu_{1S-2P} = \frac{E_{1S-2P}}{h} = 2.466710 \times 10^{15}\text{Hz} & \text{for Deuterium} \\ \nu_{1S-2P} = \frac{E_{1S-2P}}{h} = 2.466934 \times 10^{15}\text{Hz} & \text{for Tritium} \end{cases} \tag{8}$$

2.2 Relativistic Correction

The relativistic mass correction to the energy levels of the hydrogen atom is given by:

$$\Delta E_{rel}^m = -E_n \frac{Z^2 \alpha^2}{n} \left(\frac{3}{4n} - \frac{1}{l + \frac{1}{2}} \right) \tag{9}$$

where $E_n = -13.6\text{eV}$ is the non-relativistic energy level, $Z = 1$ is the atomic number, $\alpha = \frac{e^2}{\hbar c}$ is the fine structure constant, n is the principal quantum number and l is the azimuthal quantum number.

$$\begin{cases} \Delta E_{\text{rel}} = -13.6\,\text{eV} \times \frac{1^2\alpha^2}{1}\left(\frac{3}{4\times 1} - \frac{1}{\frac{1}{2}}\right) = -9.05 \times 10^{-4}\,\text{eV} & \text{for 1S} \\ \Delta E_{\text{rel}} = -13.6\,\text{eV} \times \frac{1^2\alpha^2}{2}\left(\frac{3}{4\times 2} - \frac{1}{1+\frac{1}{2}}\right) = -2.6 \times 10^{-5}\,\text{eV} & \text{for 2P} \end{cases} \tag{10}$$

The Darwin term is given by:

$$\begin{cases} \Delta E^D_{rel} = -E_n \frac{Z^2\alpha^2}{n} & \text{for } l = 0 \\ \Delta E^D_{rel} = 0 & \text{for } l \neq 0 \end{cases} \tag{11}$$

Hence, we get:

$$\begin{cases} \Delta E_{\text{Darwin}} = 7.24 \times 10^{-4}\,\text{eV} & \text{for 1S} \\ \Delta E_{\text{Darwin}} = 0 & \text{for 2P} \end{cases} \tag{12}$$

2.3 Spin-Orbit Coupling

The spin-orbit coupling is given by:

$$\Delta E_{\text{SO}} = -E_n \frac{Z^2\alpha^2}{n \cdot l(l+\frac{1}{2})(l+1)} \tag{13}$$

Therefore, we have:

$$\begin{cases} \Delta E_{\text{SO}} = 0 & \text{for 1S} \\ \Delta E_{\text{SO}} = 4.5 \times 10^{-5}\,\text{eV} & \text{for 2P} \end{cases} \tag{14}$$

2.4 Working

[1]:
```
import scipy.constants as sp
import pandas as pd
```

[2]:
```
# constant
m_e = sp.electron_mass
m_p = sp.proton_mass
m_n = sp.neutron_mass
h = sp.Planck
e_0 = sp.epsilon_0
e = sp.e
alpha = sp.fine_structure
```

[3]:
```
class Atom:
    def __init__(self, proton_num, nuetron_num, electron_num, name):
        self.pn = proton_num
        self.en = electron_num
        self.nn = nuetron_num
```

```
        self.name = name

    def compute_reduce_mass(self):
        norm = (self.nn * m_n + self.pn * m_p) * self.en * m_e
        denorm = (self.nn * m_n + self.pn * m_p) + self.en * m_e
        return norm / denorm

    def compute_energy_level_in_Joule(self, n):
        mu = self.compute_reduce_mass()
        norm = mu * e ** 4 * self.pn ** 2
        denorm = 8 * e_0**2 * h**2 * n**2
        return - norm/denorm

    def compute_energy_level_in_eV(self, n):
        return self.compute_energy_level_in_Joule(n) / e

    def determine_frequency(self, n1, n2):
        energy_level1 = self.compute_energy_level_in_Joule(n1)
        energy_level2 = self.compute_energy_level_in_Joule(n2)
        return abs(energy_level1 - energy_level2) / h

    def determine_relativistic_mass_correction(self, n, l):
        E_n = self.compute_energy_level_in_Joule(n)
        coef = (self.pn * alpha) ** 2 / n
        return - E_n * coef * (3/(4*n) - 1/(l+0.5))

    def determine_darwin_term_correction(self, n, l):
        E_n = self.compute_energy_level_in_Joule(n)
        return - E_n * (self.pn * alpha) ** 2 / n if l == 0 else 0

    def determine_spin_orbit_coupling_correction(self, n, l):
        E_n = self.compute_energy_level_in_Joule(n)
        norm = (self.pn * alpha) ** 2
        denorm = n * l * (l + 1)
        return - E_n *  norm / denorm if l != 0 else 0


H1 = Atom(1,0,1, 'Hydrogen')
D2 = Atom(1,1,1, 'Deuterium')
T3 = Atom(1,2,1, 'Tritium')
```

[4]:
```
# Q2a
atom_list = [H1, D2, T3]
table = []
for atom in atom_list:
    data = []
    data.append(atom.name)
```

```
    data.append(atom.compute_reduce_mass())
    data.append(atom.compute_energy_level_in_Joule(1))
    data.append(atom.compute_energy_level_in_Joule(1)/e)
    data.append(atom.compute_energy_level_in_Joule(2))
    data.append(atom.compute_energy_level_in_Joule(2)/e)
    data.append(atom.determine_frequency(1,2))
    table.append(data)

col_label = [
    "Atom",
    "Reduced Mass",
    "1S Energy, Joule",
    "1S Energy, eV",
    "2P Energy, Joule",
    "2P Energy, eV",
    "Absorption Frequency"
]
df = pd.DataFrame(table, columns = col_label)
df
```

[4]:

	Atom	Reduced Mass	1S Energy, Joule	1S Energy, eV	2P Energy, Joule	2P Energy, eV	Absorption Frequency
0	Hydrogen	9.104425e-31	-2.178686e-18	-13.598287	-5.446715e-19	-3.399572	2.466038e+15
1	Deuterium	9.106906e-31	-2.179279e-18	-13.601992	-5.448198e-19	-3.400498	2.466710e+15
2	Tritium	9.107732e-31	-2.179477e-18	-13.603226	-5.448693e-19	-3.400806	2.466934e+15

[5]:
```
# Q2b
atom_list = [H1]
table = []
for atom in atom_list:
    data = []
    data.append(atom.name)
    data.append(atom.determine_relativistic_mass_correction(n = 1, l = 0))
    data.append(atom.determine_relativistic_mass_correction(n = 1, l = 0)/e)
    data.append(atom.determine_darwin_term_correction(n = 1, l = 0))
    data.append(atom.determine_darwin_term_correction(n = 1, l = 0)/e)
    data.append(atom.determine_relativistic_mass_correction(n = 2, l = 1))
    data.append(atom.determine_relativistic_mass_correction(n = 2, l = 1)/e)
    data.append(atom.determine_darwin_term_correction(n = 2, l = 1))
    data.append(atom.determine_darwin_term_correction(n = 2, l = 1)/e)
    table.append(data)

col_label = [
```

```
    "Atom",
    "1S Relativistics mass increase, Joule",
    "1S Relativistics mass increase, eV",
    "1S Darwin term, Joule",
    "1S Darwin term, eV",
    "2P Relativistics mass increase, Joule",
    "2P Relativistics mass increase, eV",
    "2P Darwin term, Joule",
    "2P Darwin term, eV"
]

df = pd.DataFrame(table, columns = col_label)
df
# 0.0007245990729394214
```

[5]:
```
         Atom  1S Relativistics mass increase, Joule  \
0  Hydrogen                          -1.450225e-22

    1S Relativistics mass increase, eV  1S Darwin term, Joule  \
0                            -0.000905           1.160180e-22

    1S Darwin term, eV  2P Relativistics mass increase, Joule  \
0            0.000724                          -4.229822e-24

    2P Relativistics mass increase, eV  2P Darwin term, Joule  \
0                            -0.000026                      0

    2P Darwin term, eV
0                  0.0
```

[6]:
```
# Q2c
atom_list = [H1]
table = []
for atom in atom_list:
    data = []
    data.append(atom.name)
    data.append(atom.determine_spin_orbit_coupling_correction(n = 1, l = 0))
    data.append(atom.determine_spin_orbit_coupling_correction(n = 1, l = 0)/e)
    data.append(atom.determine_spin_orbit_coupling_correction(n = 2, l = 1))
    data.append(atom.determine_spin_orbit_coupling_correction(n = 2, l = 1)/e)
    table.append(data)

col_label = [
    "Atom",
    "1S Spin-Orbit Coupling, Joule",
    "1S Spin-Orbit Coupling, eV",
    "2P Spin-Orbit Coupling, Joule",
```

```
    "2P Spin-Orbit Coupling, eV"
]

df = pd.DataFrame(table, columns = col_label)
df
```

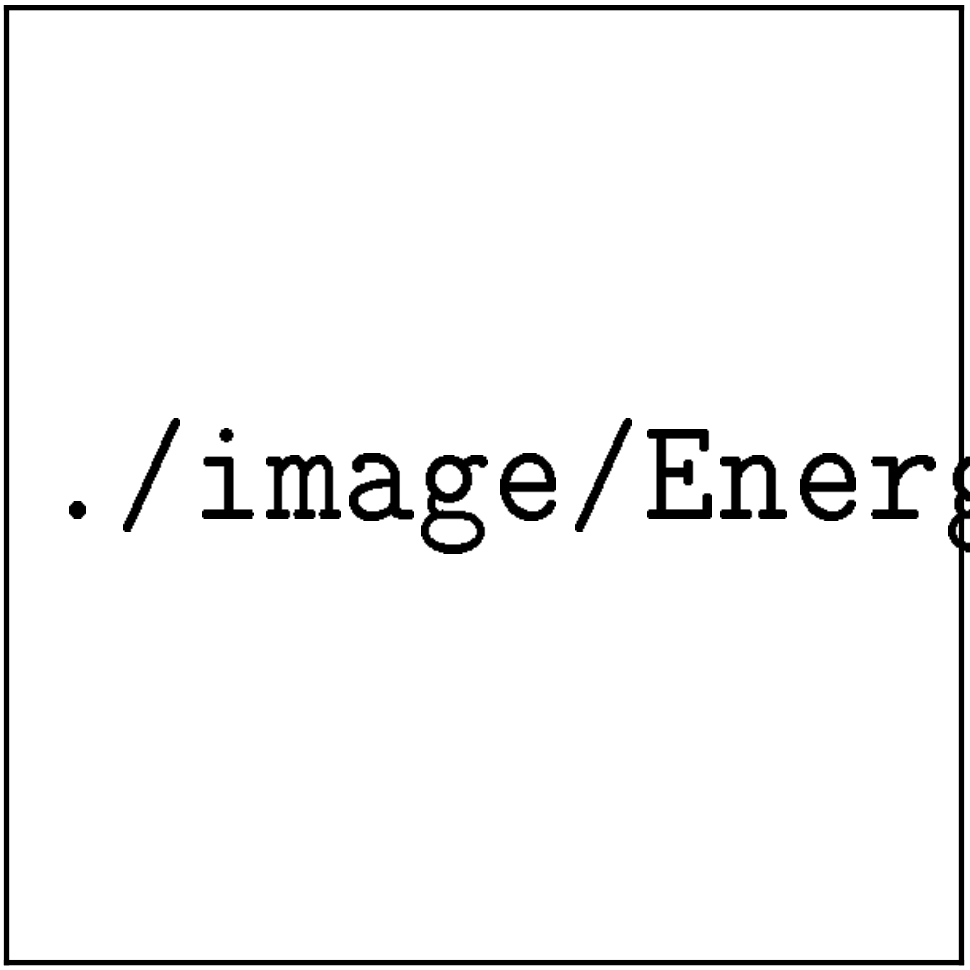
[6]:
```
        Atom  1S Spin-Orbit Coupling, Joule  1S Spin-Orbit Coupling, eV  \
0  Hydrogen                               0                          0.0

    2P Spin-Orbit Coupling, Joule  2P Spin-Orbit Coupling, eV
0                   7.251123e-24                    0.000045
```

[13]:
```
n, l = 2, 1
(H1.determine_darwin_term_correction(n,l) + H1.
 ↪determine_relativistic_mass_correction(n,l) + H1.
 ↪determine_spin_orbit_coupling_correction(n,l))/e
```

3 Hydrogen Atom

3.1 Energy Level Diagram

The scales of the corrections attributed to the fine structure and the Lamb shift are proportional to the fourth and fifth powers of the fine-structure constant, α, respectively.



3.2 Fine structure functional form

The fine structure energy interval is given by:

$$\Delta E_{n,j} = \Delta E_{n,l}^{(0)} + \Delta E_{n,l}^{(1)} + \Delta E_{n,l}^{(2)} \tag{15}$$

Subsituting the expression of $\Delta E_{n,l}^{(0)}$, $\Delta E_{n,l}^{(1)}$ and $\Delta E_{n,l}^{(2)}$ and simplify, we have:

$$\Delta E_{n,j} = -R_y^* Z^2 \left(\frac{Z^2\alpha^2}{n^3(j+\frac{1}{2})} - \frac{3Z^2\alpha^2}{4n^3} \right) \tag{16}$$

From the above expression, we can arrange the terms to get the functional form of the fine structure energy interval:

$$\Delta E_{n,j} \approx \frac{1}{4n^3} + \frac{1}{4n^3} \propto \frac{1}{n^3} \tag{17}$$

Therefore, the interval scales with $\frac{1}{n^3}$ and it is independent of the quantum number l.

3.3 Lamb Shift experime

The Lamb shift can be quantified using both Lamb Microwave Spectroscopy and Laser Spectroscopy, with each method stimulating electron transitions across different energy levels. Laser Spectroscopy stands out for its greater precision, attributed to its tighter linewidth and thus higher resolution in comparison to microwave techniques. Furthermore, Laser Spectroscopy can employ Doppler-free saturated spectroscopy methods to counteract Doppler broadening effects. On the other hand, in Microwave Spectroscopy, Doppler broadening has a more pronounced impact due to the diverse velocities of the electrons relative to the microwave radiation source