

PC3233 Assignment 6

April 2, 2024

1 Atom in magnetic fields

Consider an atom in an electronically excited fine-structure state $^4D_{1/2}$. We know that the quantum number $s = \frac{3}{2}, l = 2, j = \frac{1}{2}$.

Suppose the coupling effect of nuclear spin is negligible, the energy splitting in magnetic field is given by:

$$\Delta E = \Delta m_j g_j \mu_B B \quad (1)$$

The Lande g-factor, g_j is given by:

$$g_j = 1 + \frac{j(j+1) + s(s+1) - l(l+1)}{2j(j+1)} \quad (2)$$

Substitute the quantum numbers into the equation gives:

$$g_j = 1 + \frac{\frac{1}{2}(\frac{1}{2} + 1) + \frac{3}{2}(\frac{3}{2} + 1) - 2(2 + 1)}{2\frac{1}{2}(\frac{1}{2} + 1)} = 0 \quad (3)$$

Lande g-factor is zero, implies that the energy splitting in magnetic field is zero.

2 ^4He atom

2.1 Separable Wavefunction and Energy

From lecture, we know that the general Schrodinger equation for Helium atom is given by:

$$-\frac{\hbar^2}{2m_e} \Delta_1 \psi(\mathbf{r}_1, \mathbf{r}_2) - \frac{\hbar^2}{2m_e} \Delta_2 \psi(\mathbf{r}_1, \mathbf{r}_2) + E_{\text{pot}} \psi(\mathbf{r}_1, \mathbf{r}_2) = E \psi(\mathbf{r}_1, \mathbf{r}_2) \quad (4)$$

The E_{pot} term is the potential energy is given by:

$$E_{\text{pot}} = -\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} - \frac{1}{r_{12}} \right) \quad (5)$$

Assuming the mutual repulsion between the electrons is negligible, we can drop the $1/r_{12}$ term. Therefore, the potential energy term simplifies to:

$$E_{\text{pot}} = -\frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \quad (6)$$

Substitute the potential energy term into the Schrodinger equation gives:

$$-\frac{\hbar^2}{2m_e} \Delta_1 \psi(\mathbf{r}_1) - \frac{\hbar^2}{2m_e} \Delta_2 \psi(\mathbf{r}_2) - \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \psi(\mathbf{r}_1, \mathbf{r}_2) = E \psi(\mathbf{r}_1, \mathbf{r}_2) \quad (7)$$

Assuming the wavefunction is separable, $\psi(\mathbf{r}_1, \mathbf{r}_2) = \psi(\mathbf{r}_1)\psi(\mathbf{r}_2)$, we can rewrite the Schrodinger equation as:

$$-\frac{\hbar^2}{2m_e} \Delta_1 \psi(\mathbf{r}_1) \psi(\mathbf{r}_2) - \frac{\hbar^2}{2m_e} \Delta_2 \psi(\mathbf{r}_1) \psi(\mathbf{r}_2) - \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) \psi(\mathbf{r}_1) \psi(\mathbf{r}_2) = E \psi(\mathbf{r}_1) \psi(\mathbf{r}_2) \quad (8)$$

Dividing the equation by $\psi(\mathbf{r}_1)\psi(\mathbf{r}_2)$ gives:

$$-\frac{\hbar^2}{2m_e} \frac{\Delta_1 \psi(\mathbf{r}_1)}{\psi(\mathbf{r}_1)} - \frac{\hbar^2}{2m_e} \frac{\Delta_2 \psi(\mathbf{r}_2)}{\psi(\mathbf{r}_2)} - \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{r_1} + \frac{1}{r_2} \right) = E \quad (9)$$

Rearrange the equation gives:

$$-\frac{\hbar^2}{2m_e} \frac{\Delta_1 \psi(\mathbf{r}_1)}{\psi(\mathbf{r}_1)} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_1} - \frac{\hbar^2}{2m_e} \frac{\Delta_2 \psi(\mathbf{r}_2)}{\psi(\mathbf{r}_2)} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_2} = E_1 \quad (10)$$

The equation can be separated into two equations:

$$-\frac{\hbar^2}{2m_e} \frac{\Delta_1 \psi(\mathbf{r}_1)}{\psi(\mathbf{r}_1)} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_1} = E_1 \quad (11)$$

$$-\frac{\hbar^2}{2m_e} \frac{\Delta_2 \psi(\mathbf{r}_2)}{\psi(\mathbf{r}_2)} - \frac{e^2}{4\pi\epsilon_0} \frac{1}{r_2} = E_2 \quad (12)$$

where $E_1 + E_2 = E$.

Hence, the energy of the Helium atom is separable into two parts, E_1 and E_2 .

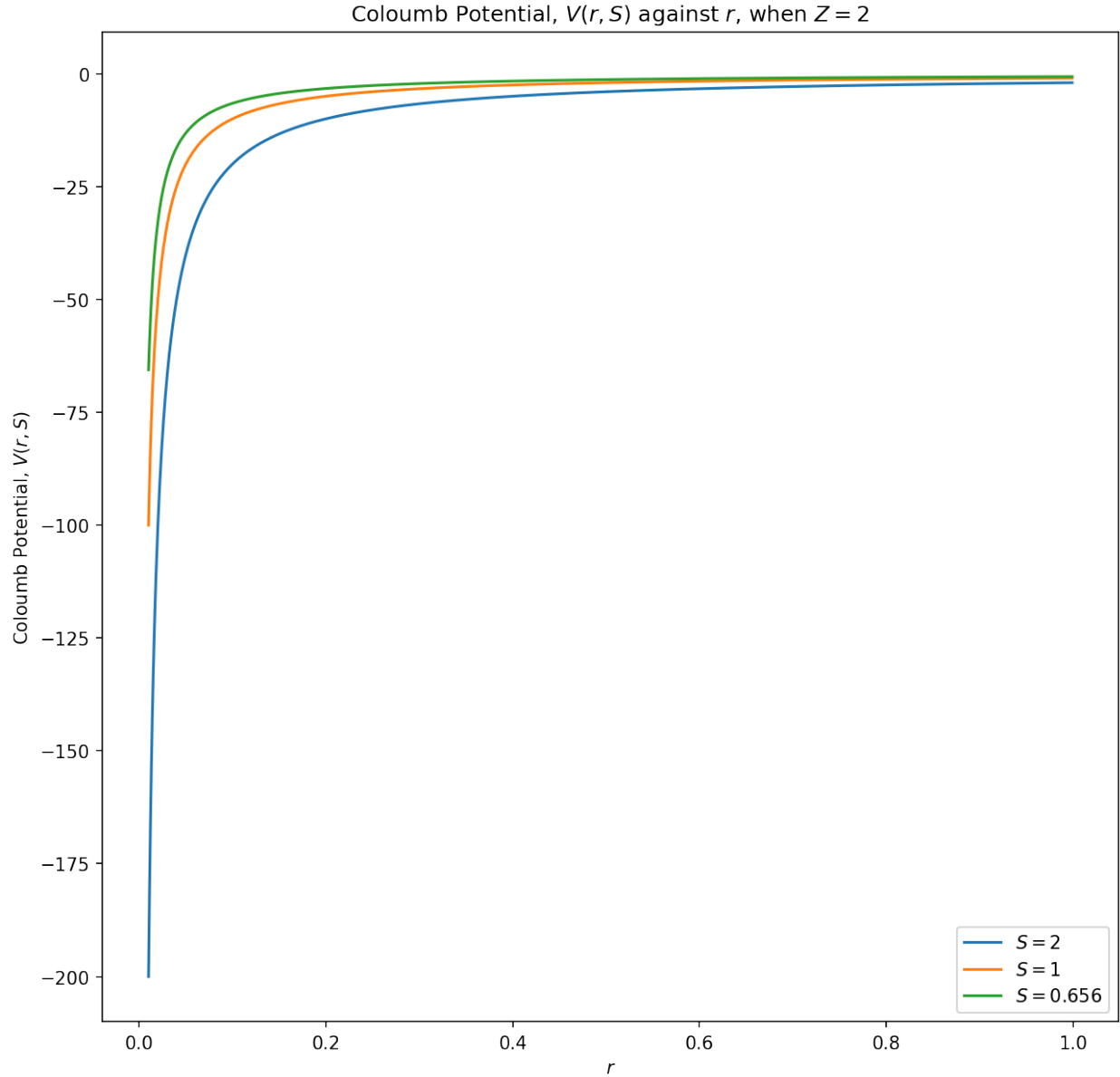
2.2 Potential Graph

Coloumb Potential is given by:

$$V(r, Z, S) = -\frac{Q_{\text{eff}}(Z, S)}{4\pi\epsilon_0} \frac{1}{r} \quad (13)$$

where $Q_{\text{eff}}(Z, S) = (Z - S)e$, S is the shielding constant.

The potential graph for the Helium atom is shown below:



3 Helium atoms

The energy to ionize a Helium atom is given by:

$$E = E_{\text{He} \rightarrow \text{He}^+} + E_{\text{He}^+ \rightarrow \text{He}^{2+}} \quad (14)$$

We already know that the ionization energy for the first electron, $E_{\text{He} \rightarrow \text{He}^+}$, is 24.6 eV. After the first electron is removed, the He^+ ion has a single electron, which is hydrogen-like. The ionization energy for the hydrogen-like atom is given by:

$$E_n = -R_y^* \frac{Z^{*2}}{n^2} \quad (15)$$

In this case, $Z^* = 2$ and $n = 1$. Therefore, the ionization energy for the He^+ ion is:

$$E_{\text{He}^+ \rightarrow \text{He}^{2+}} = -R_y^* \frac{2^2}{1^2} = -4 \times 13.6 \text{ eV} = -54.4 \text{ eV} \quad (16)$$

Hence, the total ionization energy for the Helium atom is:

$$E = 24.6 \text{ eV} + 54.4 \text{ eV} = 79 \text{ eV} \quad (17)$$

4 Two spins

Following the lecture note notation, we introduce spinor vectors

$$\chi^{m_s=+\frac{1}{2}}(\text{Hilbert Space 1}) = \chi^+(1)$$

$$\chi^{m_s=-\frac{1}{2}}(\text{Hilbert Space 1}) = \chi^-(1)$$

$$\chi^{m_s=+\frac{1}{2}}(\text{Hilbert Space 2}) = \chi^+(2)$$

$$\chi^{m_s=-\frac{1}{2}}(\text{Hilbert Space 2}) = \chi^-(2)$$

The spin function for the two electrons is given by:

$$\chi^+(1)\chi^+(2) = \chi^+(1)\chi^+(2) = |\uparrow\uparrow\rangle$$

$$\chi^+(1)\chi^-(2) = \chi^+(1)\chi^-(2) = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle)$$

$$\chi^-(1)\chi^+(2) = \chi^-(1)\chi^+(2) = \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$

$$\chi^-(1)\chi^-(2) = \chi^-(1)\chi^-(2) = |\downarrow\downarrow\rangle$$

We know that the total spin angular momentum operator is given by:

$$\mathbf{S} = \mathbf{S}(1) + \mathbf{S}(2) \quad (18)$$

To determine the expectation value of \mathbf{S}_z :

$$\langle \mathbf{S}_z \rangle = \langle \mathbf{S}_z(1) + \mathbf{S}_z(2) \rangle = \langle \mathbf{S}_z(1) \rangle + \langle \mathbf{S}_z(2) \rangle = \hbar[m_s(1) + m_s(2)] \quad (19)$$

Therefore, the expectation value of \mathbf{S}_z for single state and all the triplet states are:

$$\begin{cases} \langle \mathbf{S}_z \rangle = \hbar \left(\frac{1}{2} + \frac{1}{2} \right) = \hbar & \text{for } |\uparrow\uparrow\rangle \\ \langle \mathbf{S}_z \rangle = \hbar \left(\frac{1}{2} - \frac{1}{2} \right) = 0 & \text{for } \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\ \langle \mathbf{S}_z \rangle = \hbar \left(-\frac{1}{2} + \frac{1}{2} \right) = 0 & \text{for } \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \\ \langle \mathbf{S}_z \rangle = \hbar \left(-\frac{1}{2} - \frac{1}{2} \right) = -\hbar & \text{for } |\downarrow\downarrow\rangle \end{cases} \quad (20)$$

For \mathbf{S}^2 operator, the expectation value is given by:

$$\langle \mathbf{S}^2 \rangle = \langle \mathbf{S}^2(1) + \mathbf{S}^2(2) + 2\mathbf{S}(1) \cdot \mathbf{S}(2) \rangle \quad (21)$$

$$= \langle \mathbf{S}^2(1) \rangle + \langle \mathbf{S}^2(2) \rangle + 2\langle \mathbf{S}(1) \cdot \mathbf{S}(2) \rangle \quad (22)$$

Since $\mathbf{S}(i) = \mathbf{S}_x(i) + \mathbf{S}_y(i) + \mathbf{S}_z(i)$, the dot product of $\mathbf{S}(1)$ and $\mathbf{S}(2)$ is given by:

$$\mathbf{S}(1) \cdot \mathbf{S}(2) = \mathbf{S}_x(1)\mathbf{S}_x(2) + \mathbf{S}_y(1)\mathbf{S}_y(2) + \mathbf{S}_z(1)\mathbf{S}_z(2) \quad (23)$$

We know that $\mathbf{S}_x = \frac{\mathbf{S}_+ + \mathbf{S}_-}{2}$, $\mathbf{S}_y = \frac{\mathbf{S}_+ - \mathbf{S}_-}{2i}$, and $\mathbf{S}_z = \frac{\mathbf{S}_+ \mathbf{S}_-}{\hbar}$. Therefore, we can rewrite the expression in (22) as:

$$\begin{aligned} & \langle \mathbf{S}^2(1) \rangle + \langle \mathbf{S}^2(2) \rangle + 2\langle \mathbf{S}(1) \cdot \mathbf{S}(2) \rangle \\ &= \langle \mathbf{S}^2(1) \rangle + \langle \mathbf{S}^2(2) \rangle + 2\langle \mathbf{S}_x(1)\mathbf{S}_x(2) + \mathbf{S}_y(1)\mathbf{S}_y(2) + \mathbf{S}_z(1)\mathbf{S}_z(2) \rangle \\ &= \langle \mathbf{S}^2(1) \rangle + \langle \mathbf{S}^2(2) \rangle + 2\langle \frac{\mathbf{S}_+(1) + \mathbf{S}_-(1)}{2} \frac{\mathbf{S}_+(2) + \mathbf{S}_-(2)}{2} + \frac{\mathbf{S}_+(1) - \mathbf{S}_-(1)}{2i} \frac{\mathbf{S}_+(2) - \mathbf{S}_-(2)}{2i} + \mathbf{S}_z(1)\mathbf{S}_z(2) \rangle \end{aligned}$$

Since $\mathbf{S}_+ |\uparrow\rangle = 0$, $\mathbf{S}_- |\downarrow\rangle = 0$, and $\mathbf{S}_+ |\downarrow\rangle = \mathbf{S}_- |\uparrow\rangle = \frac{\hbar^2}{2}$.

We can then compute the expectation value of \mathbf{S}^2 for each state:

$$\begin{cases} \langle \mathbf{S}^2 \rangle = 2\hbar^2 & \text{for } |\uparrow\uparrow\rangle \\ \langle \mathbf{S}^2 \rangle = 2\hbar^2 & \text{for } \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle + |\downarrow\uparrow\rangle) \\ \langle \mathbf{S}^2 \rangle = 0 & \text{for } \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle) \\ \langle \mathbf{S}^2 \rangle = 2\hbar^2 & \text{for } |\downarrow\downarrow\rangle \end{cases} \quad (24)$$