

PYU33P15: Atomic Physics

Problem Set 2 due 09/12/2021

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Q1

(a)

$$\begin{aligned} 1 &= |\chi| \\ &= |A| \sqrt{3^2 + 4^2} \\ &= 5 |A| \\ \implies |A| &= \frac{1}{5} \end{aligned}$$

(b)

$$S_x = \frac{\hbar}{2} (|1\rangle \langle 2| + |2\rangle \langle 1|) \quad S_y = \frac{\hbar}{2} (-i |1\rangle \langle 2| + i |2\rangle \langle 1|) \quad S_z = \frac{\hbar}{2} (|1\rangle \langle 1| - |2\rangle \langle 2|)$$

$$\begin{aligned} \langle S_x \rangle_\chi &= A^* (-3i \langle 1| + 4 \langle 2|) \frac{\hbar}{2} (|1\rangle \langle 2| + |2\rangle \langle 1|) A (3i |1\rangle + 4 |2\rangle) \\ &= A^* A \frac{\hbar}{2} (-3i \langle 2| + 4 \langle 1|) (3i |1\rangle + 4 |2\rangle) \\ &= |A|^2 \frac{\hbar}{2} (-12i + 12i) \\ \langle S_x \rangle_\chi &= 0 \end{aligned}$$

$$\begin{aligned} \langle S_y \rangle_\chi &= A^* (-3i \langle 1| + 4 \langle 2|) \frac{\hbar}{2} (-i |1\rangle \langle 2| + i |2\rangle \langle 1|) A (3i |1\rangle + 4 |2\rangle) \\ &= A^* A \frac{\hbar}{2} (-3 \langle 2| + 4i \langle 1|) (3i |1\rangle + 4 |2\rangle) \\ &= |A|^2 \frac{\hbar}{2} (-12 - 12) \\ &= \frac{1}{25} \frac{\hbar}{2} (-24) \\ \langle S_y \rangle_\chi &= -\frac{12\hbar}{25} \end{aligned}$$

$$\begin{aligned} \langle S_z \rangle_\chi &= A^* (-3i \langle 1| + 4 \langle 2|) \frac{\hbar}{2} (|1\rangle \langle 1| - |2\rangle \langle 2|) A (3i |1\rangle + 4 |2\rangle) \\ &= A^* A \frac{\hbar}{2} (-3i \langle 1| - 4 \langle 2|) (3i |1\rangle + 4 |2\rangle) \\ &= |A|^2 \frac{\hbar}{2} (9 - 16) \\ &= \frac{1}{25} \frac{\hbar}{2} (-7) \\ \langle S_z \rangle_\chi &= -\frac{7\hbar}{50} \end{aligned}$$

(c)

$$\begin{aligned}
S_i^2 &= \left(\frac{\hbar}{2} \sigma_i \right)^2 \\
&= \frac{\hbar^2}{4} I \\
\Rightarrow \langle S_i^2 \rangle_\chi &= \chi^* \frac{\hbar^2}{4} I \chi \\
&= \frac{\hbar^2}{4} |\chi|^2 \\
&= \frac{\hbar^2}{4} \\
\Rightarrow \langle S_x^2 \rangle_\chi &= \langle S_y^2 \rangle_\chi = \langle S_z^2 \rangle_\chi = \frac{\hbar^2}{4}
\end{aligned}$$

$$\begin{aligned}
\Delta S_x &= \sqrt{\langle S_x^2 \rangle_\chi - \langle S_x \rangle_\chi^2} & \Delta S_y &= \sqrt{\langle S_y^2 \rangle_\chi - \langle S_y \rangle_\chi^2} & \Delta S_z &= \sqrt{\langle S_z^2 \rangle_\chi - \langle S_z \rangle_\chi^2} \\
&= \sqrt{\frac{\hbar^2}{4} - 0^2} & &= \sqrt{\frac{\hbar^2}{4} - \frac{144 \hbar^2}{625}} & &= \sqrt{\frac{\hbar^2}{4} - \frac{49 \hbar^2}{2500}} \\
\Delta S_x &= \frac{\hbar}{2} & \Delta S_y &= \frac{7 \hbar}{50} & \Delta S_z &= \frac{12 \hbar}{25}
\end{aligned}$$

(d)

$$\text{Uncertainty relation: } \Delta \hat{A} \Delta \hat{B} \geq \frac{1}{2} \left| \langle [\hat{A}, \hat{B}] \rangle \right|$$

$$[S_i, S_i] = 0 \Rightarrow \text{relation holds for } S_i \text{ and } S_i$$

$$\begin{aligned}
\Delta S_x \Delta S_y &= \frac{\hbar}{2} \frac{7 \hbar}{50} & \Delta S_y \Delta S_z &= \frac{7 \hbar}{50} \frac{12 \hbar}{25} & \Delta S_z \Delta S_x &= \frac{12 \hbar}{25} \frac{\hbar}{2} \\
&= \frac{7 \hbar^2}{100} & &= \frac{42 \hbar^2}{625} & &= \frac{6 \hbar^2}{25} \\
\frac{1}{2} |\langle [S_x, S_y] \rangle| &= \frac{1}{2} |\langle i \hbar S_z \rangle| & \frac{1}{2} |\langle [S_y, S_z] \rangle| &= \frac{1}{2} |\langle i \hbar S_x \rangle| & \frac{1}{2} |\langle [S_z, S_x] \rangle| &= \frac{1}{2} |\langle i \hbar S_y \rangle| \\
&= \frac{1}{2} \left| i \hbar \left(-\frac{7 \hbar}{50} \right) \right| & &= \frac{1}{2} |i \hbar (0)| & &= \frac{1}{2} \left| i \hbar \left(-\frac{12 \hbar}{25} \right) \right| \\
&= \frac{7 \hbar^2}{100} & &= 0 & &= \frac{6 \hbar^2}{25} \\
\Delta S_x \Delta S_y &= \frac{1}{2} |\langle [S_x, S_y] \rangle| & \Delta S_y \Delta S_z &> \frac{1}{2} |\langle [S_y, S_z] \rangle| & \Delta S_z \Delta S_x &= \frac{1}{2} |\langle [S_z, S_x] \rangle|
\end{aligned}$$

Thus the results in (c) are consistent with uncertainty relations.

Q2

(a)

$$\begin{aligned} 0 &= \det(S_y - \lambda I) \\ &= \begin{vmatrix} -\lambda & -\frac{i\hbar}{2} \\ \frac{i\hbar}{2} & -\lambda \end{vmatrix} \\ &= \lambda^2 - \frac{\hbar^2}{4} \\ \implies \lambda &= \pm \frac{\hbar}{2} \end{aligned}$$

$$\begin{aligned} S_y \vec{x} &= \lambda \vec{x} \\ \implies 0 &= (S_y - \lambda I) \vec{x} \\ &= \begin{pmatrix} \mp \frac{\hbar}{2} & -\frac{i\hbar}{2} \\ \frac{i\hbar}{2} & \mp \frac{\hbar}{2} \end{pmatrix} \vec{x} \\ &= -\frac{\hbar}{2} \begin{pmatrix} \pm 1 & i \\ -i & \pm 1 \end{pmatrix} \begin{pmatrix} x_1 \\ x_2 \end{pmatrix} \\ \implies 0 &= \pm x_1 + i x_2 \\ \implies x_2 &= \pm i x_1 \\ \implies \vec{x} &= A \begin{pmatrix} 1 \\ \pm i \end{pmatrix} \\ \vec{x} \text{ normalised} &\implies \vec{x} = \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ \pm i \end{pmatrix} \end{aligned}$$

Thus the eigenvectors and corresponding eigenvalues of S_y are

$$\begin{aligned} \vec{x}_+ &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ i \end{pmatrix} & \vec{x}_- &= \frac{1}{\sqrt{2}} \begin{pmatrix} 1 \\ -i \end{pmatrix} \\ \lambda_+ &= \frac{\hbar}{2} & \lambda_- &= -\frac{\hbar}{2} \end{aligned}$$

(b)

$$\begin{aligned}
\vec{\chi} &= \begin{pmatrix} \alpha \\ \beta \end{pmatrix} \\
&= \gamma \vec{x}_+ + \delta \vec{x}_- \quad (\text{expressing } \chi \text{ as a linear combination of the eigenvectors of } S_y) \\
&= \frac{1}{\sqrt{2}} \begin{pmatrix} \gamma + \delta \\ i(\gamma - \delta) \end{pmatrix} \\
\Rightarrow \alpha &= \frac{\gamma + \delta}{\sqrt{2}}, \beta = \frac{i(\gamma - \delta)}{\sqrt{2}} \\
\Rightarrow \gamma &= \frac{\alpha - i\beta}{\sqrt{2}}, \delta = \frac{\alpha + i\beta}{\sqrt{2}} \\
\Rightarrow \vec{\chi} &= \frac{\alpha - i\beta}{\sqrt{2}} \vec{x}_+ + \frac{\alpha + i\beta}{\sqrt{2}} \vec{x}_-
\end{aligned}$$

$$\begin{aligned}
P\left(\frac{\hbar}{2}\right) &= \langle \chi | x_+ \rangle \langle x_+ | \chi \rangle & P\left(-\frac{\hbar}{2}\right) &= \langle \chi | x_- \rangle \langle x_- | \chi \rangle \\
&= \left(\frac{\alpha - i\beta}{\sqrt{2}}\right)^* \frac{\alpha - i\beta}{\sqrt{2}} + 0 & &= 0 + \left(\frac{\alpha + i\beta}{\sqrt{2}}\right)^* \frac{\alpha + i\beta}{\sqrt{2}} \quad (\text{since } \vec{x}_+, \vec{x}_- \text{ are orthogonal}) \\
&= \frac{|\alpha - i\beta|^2}{2} & &= \frac{|\alpha + i\beta|^2}{2}
\end{aligned}$$

Thus for a state χ given by $\vec{\chi} = \begin{pmatrix} \alpha \\ \beta \end{pmatrix}$, the probability of measuring $\frac{\hbar}{2}$ is $\frac{|\alpha - i\beta|^2}{2}$, and the probability of measuring $-\frac{\hbar}{2}$ is $\frac{|\alpha + i\beta|^2}{2}$.

The sum of these probabilities is $\frac{|\alpha - i\beta|^2}{2} + \frac{|\alpha + i\beta|^2}{2} = |\gamma|^2 + |\delta|^2$. Since $\vec{\chi}$ is normalised, we then have that $|\vec{\chi}|^2 = |\gamma|^2 + |\delta|^2 = 1$, since $\vec{x}_+$ and $\vec{x}_-$ are orthonormal vectors. Therefore the probabilities $P\left(\frac{\hbar}{2}\right)$ and $P\left(-\frac{\hbar}{2}\right)$ add to 1.

(c)

We have from before that $S_y^2 = \frac{\hbar^2}{4} I$, and thus its only eigenvalue is $\frac{\hbar^2}{4}$, corresponding to any non-zero vector as its eigenvector. Thus, for a given state χ , $\vec{\chi}$ will be an eigenvector of S_y^2 . Therefore,

$$\begin{aligned}
P\left(\frac{\hbar^2}{4}\right) &= \langle \chi | \chi \rangle \langle \chi | \chi \rangle \\
&= 1 \text{ if } \vec{\chi} \text{ is normalised,}
\end{aligned}$$

and so the probability of measuring $\frac{\hbar^2}{4}$ is 1.

Q3

$$\begin{aligned}
 \vec{\mu}_L &= -\frac{e}{2m_e} \vec{L} \\
 |\mu_L| &= \left| -\frac{e}{2m_e} \vec{L} \right| \\
 &= \frac{e}{2m_e} \sqrt{\hbar^2 \ell(\ell-1)} \\
 &= \frac{\hbar e}{2m_e} \sqrt{\ell(\ell-1)} \\
 p\text{-orbital} &\implies \ell = 2 \\
 \implies |\mu_L| &= \frac{\hbar e}{2m_e} \sqrt{2(2-1)} \\
 &= \frac{\hbar e}{m_e \sqrt{2}} \approx 1.311 \times 10^{-23} \text{ A} \cdot \text{m}^2
 \end{aligned}$$

Q4

(a)

$$\begin{aligned}
 E_n &= \frac{E_1}{n^2} \\
 \Delta E_{n \rightarrow m} &= E_n - E_m \\
 &= E_1 \left(\frac{1}{n^2} - \frac{1}{m^2} \right) \\
 \Delta E_{3 \rightarrow 2} &= E_1 \left(\frac{1}{3^2} - \frac{1}{2^2} \right) \\
 &= -\frac{5 E_1}{36} \\
 \lambda_{3 \rightarrow 2} &= \frac{h c}{\Delta E_{3 \rightarrow 2}} \\
 \lambda_{3 \rightarrow 2} &= -\frac{36 h c}{5 E_1} \approx 656.470 \text{ nm} \\
 f_{3 \rightarrow 2} &= \frac{c}{\lambda_{3 \rightarrow 2}} \\
 f_{3 \rightarrow 2} &= -\frac{5 E_1}{36 h} \approx 4.567 \times 10^{14} \text{ Hz}
 \end{aligned}$$

(b)

$$\begin{aligned}
E'_r + E'_{\text{SO}} &= \frac{E_n^2}{2mc^2} \left(3 - \frac{4n}{l + \frac{1}{2}} + \frac{2n(j(j+1) - l(l+1) - \frac{3}{4})}{l(l + \frac{1}{2})(l+1)} \right) \\
&= \frac{E_n^2}{2mc^2} \left(3 + \frac{-4nl(l+1) + 2nj(j+1) - 2nl(l+1) - \frac{3}{2}n}{l(l + \frac{1}{2})(l+1)} \right) \\
&= \frac{E_n^2}{2mc^2} \left(3 + \frac{2nj(j+1) - 6nl(l+1) - \frac{3}{2}n}{l(l + \frac{1}{2})(l+1)} \right) \\
&= \frac{E_n^2}{2mc^2} \left(3 + \frac{4n}{j + \frac{1}{2}} \frac{\frac{1}{2}j(j+1) - \frac{3}{2}l(l+1) - \frac{3}{8}}{l(l + \frac{1}{2})(l+1)} \left(j + \frac{1}{2} \right) \right) \\
&= \frac{E_n^2}{2mc^2} \left(3 + \frac{4n}{j + \frac{1}{2}} f(j, l) \right)
\end{aligned}$$

$$j = l + s = l \pm \frac{1}{2}$$

$$\begin{aligned}
f\left(l + \frac{1}{2}, l\right) &= \frac{\frac{1}{2}(l + \frac{1}{2})(l + \frac{3}{2}) - \frac{3}{2}l(l+1) - \frac{3}{8}}{l(l + \frac{1}{2})(l+1)} (l+1) & f\left(l - \frac{1}{2}, l\right) &= \frac{\frac{1}{2}(l - \frac{1}{2})(l + \frac{1}{2}) - \frac{3}{2}l(l+1) - \frac{3}{8}}{l(l + \frac{1}{2})(l+1)} l \\
&= \frac{\frac{1}{2}(l^2 + 2l + \frac{3}{4}) - \frac{3}{2}(l^2 + l) - \frac{3}{8}}{l(l + \frac{1}{2})} & &= \frac{\frac{1}{2}(l^2 - \frac{1}{4}) - \frac{3}{2}(l^2 + l) - \frac{3}{8}}{(l + \frac{1}{2})(l+1)} \\
&= \frac{\frac{1}{2}l^2 + l + \frac{3}{8} - \frac{3}{2}l^2 - \frac{3}{2}l - \frac{3}{8}}{l^2 + \frac{1}{2}l} & &= \frac{\frac{1}{2}l^2 - \frac{1}{8} - \frac{3}{2}l^2 - \frac{3}{2}l - \frac{3}{8}}{l^2 + \frac{3}{2}l + \frac{1}{2}} \\
&= \frac{-l^2 - \frac{1}{2}l}{l^2 + \frac{1}{2}l} & &= \frac{-l^2 - \frac{3}{2}l - \frac{1}{2}}{l^2 + \frac{3}{2}l + \frac{1}{2}} \\
&= -1 & &= -1
\end{aligned}$$

$$\implies f(j, l) = -1 \text{ for } j = l \pm \frac{1}{2}$$

$$\implies E'_r + E'_{\text{SO}} = \frac{E_n^2}{2mc^2} \left(3 - \frac{4n}{j + \frac{1}{2}} \right)$$

(c)

(i)

For $n = 2$, we have that $j = l + s = 0 \pm \frac{1}{2}, 1 \pm \frac{1}{2} = -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}$. For $n = 3$, we have that $j = l + s = 0 \pm \frac{1}{2}, 1 \pm \frac{1}{2}, 2 \pm \frac{1}{2} = -\frac{1}{2}, \frac{1}{2}, \frac{3}{2}, \frac{5}{2}$. However, from inspecting the correction term, a singularity arises whenever $j = -\frac{1}{2}$, and thus the allowable values of j are $\frac{1}{2}$ and $\frac{3}{2}$ for $n = 2$, and $\frac{1}{2}$, $\frac{3}{2}$ and $\frac{5}{2}$ for $n = 3$. Therefore [there are six possible lines in the Balmer series](#), for the energy transition $3 \rightarrow 2$.

(ii)

$$\begin{aligned}
E_n &= \frac{E_1}{n^2} + \frac{E_1^2}{2n^4 m c^2} \left(3 - \frac{4n}{j_n + \frac{1}{2}} \right) \\
\Delta E_{j_2, j_3} &= E_3 - E_2 \\
&= \frac{E_1}{3^2} + \frac{E_1^2}{2(3^4) m c^2} \left(3 - \frac{4(3)}{j_3 + \frac{1}{2}} \right) - \frac{E_1}{2^2} - \frac{E_1^2}{2(2^4) m c^2} \left(3 - \frac{4(2)}{j_2 + \frac{1}{2}} \right) \\
&= -\frac{5E_1}{36} + \frac{E_1^2}{m c^2} \left(\frac{1}{4(j_2 + \frac{1}{2})} - \frac{2}{27(j_3 + \frac{1}{2})} - \frac{65}{864} \right) \\
&= -\frac{5E_1}{36} + \frac{E_1^2}{m c^2} g(j_2, j_3)
\end{aligned}$$

$$\begin{aligned}
g\left(\frac{1}{2}, \frac{1}{2}\right) &= \frac{29}{288} & g\left(\frac{1}{2}, \frac{3}{2}\right) &= \frac{119}{864} & g\left(\frac{1}{2}, \frac{5}{2}\right) &= \frac{389}{2592} \\
g\left(\frac{3}{2}, \frac{1}{2}\right) &= -\frac{7}{288} & g\left(\frac{3}{2}, \frac{3}{2}\right) &= \frac{11}{864} & g\left(\frac{3}{2}, \frac{5}{2}\right) &= \frac{65}{2592}
\end{aligned}$$

$$\lambda_{j_2, j_3} = \frac{h c}{\Delta E_{j_2, j_3}}$$

$$\begin{aligned}
\lambda_{\frac{1}{2}, \frac{1}{2}} &= 656.45693 \text{ nm} & \lambda_{\frac{1}{2}, \frac{3}{2}} &= 656.45227 \text{ nm} & \lambda_{\frac{1}{2}, \frac{5}{2}} &= 656.45072 \text{ nm} \\
\lambda_{\frac{3}{2}, \frac{1}{2}} &= 656.47266 \text{ nm} & \lambda_{\frac{3}{2}, \frac{3}{2}} &= 656.46800 \text{ nm} & \lambda_{\frac{3}{2}, \frac{5}{2}} &= 656.46645 \text{ nm}
\end{aligned}$$

$$f_{j_2, j_3} = \frac{\Delta E_{j_2, j_3}}{h}$$

$$\begin{aligned}
f_{\frac{1}{2}, \frac{1}{2}} &= 4.5668260 \times 10^{14} \text{ Hz} & f_{\frac{1}{2}, \frac{3}{2}} &= 4.5668584 \times 10^{14} \text{ Hz} & f_{\frac{1}{2}, \frac{5}{2}} &= 4.5668692 \times 10^{14} \text{ Hz} \\
f_{\frac{3}{2}, \frac{1}{2}} &= 4.5667166 \times 10^{14} \text{ Hz} & f_{\frac{3}{2}, \frac{3}{2}} &= 4.5667490 \times 10^{14} \text{ Hz} & f_{\frac{3}{2}, \frac{5}{2}} &= 4.5667598 \times 10^{14} \text{ Hz}
\end{aligned}$$

$\Delta\lambda = 0.00155 \text{ nm}$ $\Delta f = 1.08 \times 10^9 \text{ Hz}$	$\Delta\lambda = 0.00466 \text{ nm}$ $\Delta f = 3.24 \times 10^9 \text{ Hz}$	$\Delta\lambda = 0.00952 \text{ nm}$ $\Delta f = 6.62 \times 10^9 \text{ Hz}$	$\Delta\lambda = 0.00155 \text{ nm}$ $\Delta f = 1.08 \times 10^9 \text{ Hz}$	$\Delta\lambda = 0.00466 \text{ nm}$ $\Delta f = 3.24 \times 10^9 \text{ Hz}$
$j_2 = \frac{1}{2}, j_3 = \frac{5}{2}$	$j_2 = \frac{1}{2}, j_3 = \frac{3}{2}$	$j_2 = \frac{1}{2}, j_3 = \frac{1}{2}$	$j_2 = \frac{3}{2}, j_3 = \frac{5}{2}$	$j_2 = \frac{3}{2}, j_3 = \frac{3}{2}$
	$j_2 = \frac{3}{2}, j_3 = \frac{1}{2}$			$j_2 = \frac{5}{2}, j_3 = \frac{1}{2}$

Q5

$$\begin{aligned}\langle H \rangle &= \left(2 Z^2 - 4 Z (Z - Z_0) - \frac{5}{4} Z \right) E_1 \\ &= \left(-2 Z^2 + \left(4 Z_0 - \frac{5}{4} \right) Z \right) E_1\end{aligned}$$

$$\begin{aligned}0 &= \frac{d \langle H \rangle}{dZ} \\ &= \left(-4 Z + 4 Z_0 - \frac{5}{4} \right) E_1 \\ \implies Z &= Z_0 - \frac{5}{16}\end{aligned}$$

$$\begin{aligned}\implies \langle H \rangle &= \left(-2 \left(Z_0 - \frac{5}{16} \right)^2 + \left(4 Z_0 - \frac{5}{4} \right) \left(Z_0 - \frac{5}{16} \right) \right) E_1 \\ &= \left(-2 \left(Z_0 - \frac{5}{16} \right)^2 + 4 \left(Z_0 - \frac{5}{16} \right)^2 \right) E_1 \\ &= 2 E_1 \left(Z_0 - \frac{5}{16} \right)^2 \\ &\approx -196.431 \text{ eV for } Z_0 = 3\end{aligned}$$

The experimental ground state of energy is -198.09 eV ,¹ and so the calculated value deviates less than 1% from the experimental value. This is much lower than the deviation that would be calculated assuming the electrons have no interactions, indicating that the variational approach is a good method of solving ground state energies.

¹Kramida, A., Ralchenko, Yu., Reader, J., and NIST ASD Team (2021). NIST Atomic Spectra Database (ver. 5.9), [Online]. Available: <https://physics.nist.gov/asd> [2021, December 6]. National Institute of Standards and Technology, Gaithersburg, MD. DOI: <https://doi.org/10.18434/T4W30F>