Tutorial 6: Solutions

1. Mass-velocity term in the fine structure of the hydrogen atomic spectrum

(a)

$$\begin{aligned}
KE_{rel} &= (p^2c^2 + m_e^2c^4)^{1/2} - m_ec^2 \\
&= m_ec^2\Big(1 + \frac{p^2}{m_e^2c^2}\Big)^{1/2} - m_ec^2 \\
&\approx m_ec^2\Big(1 + \frac{1}{2}\frac{p^2}{m_e^2c^2} + \frac{(\frac{1}{2})(-\frac{1}{2})}{2!}\big(\frac{p^2}{m_e^2c^2}\big)^2 + \cdots\Big) - m_ec^2 \\
&= \frac{p^2}{2m_e} - \frac{1}{8}\frac{p^4}{m_e^3c^2} + \cdots
\end{aligned}$$

The first order correction to the non-relativistic KE, $\frac{p^2}{2m_e}$ is

$$V = -\frac{p^4}{8m_e^3c^2}$$

which is the mass-velocity term in Dirac's equation.
(Comment: In the non-relativistic limit, $(\frac{p}{m_ec})^2$ is small.)

(b) We need to use degenerate perturbation theory, since $|n\ell m_\ell\rangle$ have degenerate eigenvalues for the operator H_0.
Since V is rotationally invariant,

$$[V, L^2] = [V, L_z] = 0$$
$$\therefore \langle n\ell m_\ell|V|n\ell' m_{\ell'}\rangle \propto \delta_{\ell\ell'}\delta_{m_\ell m_{\ell'}}$$

Note also that $|n\ell m_\ell\rangle$ have distinct non-degenerate eigenvalues for the operators L^2 and L_z.
So using the basis $\{|n\ell m\rangle\}$, V is diagonal in the degenerate subspace for each n. Thus, the first order correction is given by

$$E_{rel} = \langle n\ell m_\ell|V|n\ell m_\ell\rangle.$$

From Eq. (6),

$$
\begin{aligned}
p^2|n\ell m\rangle &= 2m_e\big(E_n + \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}\big)|n\ell m\rangle \\
\langle n\ell m|p^4|n\ell m\rangle &= \langle n\ell m|p^2\cdot p^2|n\ell m\rangle \\
&= \langle n\ell m|\Big(2m_e\big(E_n + \frac{e^2}{4\pi\epsilon_0}\frac{1}{r}\big)\Big)^2|n\ell m\rangle \\
&= 4m_e^2\langle n\ell m|E_n^2 + 2E_n\frac{e^2}{4\pi\epsilon_0}\frac{1}{r} + \big(\frac{e^2}{4\pi\epsilon_0}\big)^2\frac{1}{r^2}\big)|n\ell m\rangle \\
&= 4m_e^2\Big(E_n^2 + 2E_n\frac{e^2}{4\pi\epsilon_0}\Big\langle\frac{1}{r}\Big\rangle + \big(\frac{e^2}{4\pi\epsilon_0}\big)^2\Big\langle\frac{1}{r^2}\Big\rangle\Big)
\end{aligned}
$$

Thus

$$
\begin{aligned}
E_{rel} &= -\frac{1}{8m_e^3c^2}\langle n\ell m|p^4|n\ell m\rangle \\
&= -\frac{1}{2m_ec^2}\Big(E_n^2 + 2E_n\frac{e^2}{4\pi\epsilon_0}\Big\langle\frac{1}{r}\Big\rangle + \big(\frac{e^2}{4\pi\epsilon_0}\big)^2\Big\langle\frac{1}{r^2}\Big\rangle\Big)
\end{aligned}
$$

(c)

$$
\begin{aligned}
\Big\langle\frac{1}{r}\Big\rangle &= \frac{1}{a_0n^2} \\
\Big\langle\frac{1}{r^2}\Big\rangle &= \frac{1}{(\ell+1/2)a_0^2n^3},
\end{aligned}
$$

$$
\begin{aligned}
E_{rel} &= -\frac{1}{2m_ec^2}\Big(E_n^2 + 2E_n\frac{e^2}{4\pi\epsilon_0}\frac{1}{a_0n^2} + \big(\frac{e^2}{4\pi\epsilon_0}\big)^2\frac{1}{(\ell+1/2)a_0^2n^3}\Big) \\
&\text{use } E_n = -\frac{1}{4\pi\epsilon_0}\frac{e^2}{2a_0}\frac{1}{n^2} \\
E_{rel} &= -\frac{1}{2m_ec^2}\Big(E_n^2 - 4E_n\big(-\frac{e^2}{4\pi\epsilon_0 2a_0n^2}\big) + \big(\frac{e^2}{4\pi\epsilon_0}\big)^2\frac{1}{4a_0^2n^4}\frac{4n}{(\ell+1/2)}\Big) \\
&= -\frac{1}{2m_ec^2}\Big(E_n^2 - 4E_n^2 + E_n^2\frac{4n}{(\ell+1/2)}\Big) \\
&= -\frac{E_n^2}{2m_ec^2}\Big(\frac{4n}{(\ell+1/2)} - 3\Big)
\end{aligned}
$$

(d)

$$
\begin{aligned}
\text{Use } E_n &= -\frac{1}{2}\alpha^2m_ec^2\frac{1}{n^2} \\
E_{rel} &= \frac{E_n}{2m_ec^2}\Big(\frac{1}{2}\frac{\alpha^2m_ec^2}{n^2}\Big)\Big(\frac{4n}{(\ell+1/2)} - 3\Big) \\
&= E_n\frac{\alpha^2}{n^2}\Big(\frac{n}{(\ell+1/2)} - \frac{3}{4}\Big)
\end{aligned}
$$

(Comment: For questions such as 3c and 3d, you need to show the steps. Please do not just repeat the statement in the question, as this is not answering the question.)

2. Spin-orbit coupling correction to the ground state energy of the hydrogen atom

(a) From Question 3 of Tutorial 2.2, $\vec{J}^2$, J_z, $\vec{L}^2$ and $\vec{S}^2$ commute with U.
Also, the eigenvalues of $\vec{J}^2$, J_z, $\vec{L}^2$ and $\vec{S}^2$ are distinct for distinct $|n, j, m_j, \ell, s\rangle$.
Thus U is diagonal in the basis of $|n, j, m_j, \ell, s\rangle$.

(b) Note that

$$|n, j = \frac{1}{2}, m_j, \ell = 0, s = \frac{1}{2}\rangle = |n, \ell = 0, m_\ell\rangle \otimes |s = \frac{1}{2}, m_s\rangle. \tag{1}$$

(1) is an eigenstate of H_0.

$$\begin{aligned}
\vec{S} \cdot \vec{L} &= \frac{1}{2}(\vec{J}^2 - \vec{S}^2 - \vec{L}^2) \\
&\vec{S} \cdot \vec{L}|n, j = \frac{1}{2}, m_j, \ell = 0, s = \frac{1}{2}\rangle \\
&= \frac{\hbar^2}{2}\Big(j(j+1) - s(s+1) - \ell(\ell+1)\Big)|n, j = \frac{1}{2}, m_j, \ell = 0, s = \frac{1}{2}\rangle \\
&= \frac{\hbar^2}{2}\Big(\frac{1}{2}(\frac{1}{2}+1) - \frac{1}{2}(\frac{1}{2}+1) - 0\Big)|n, j = \frac{1}{2}, m_j, \ell = 0, s = \frac{1}{2}\rangle \\
&= 0
\end{aligned}$$

Thus, (1) is also an eigenstate of H with the same eigenvalue (no correction from U).

(c) For $\ell \neq 0$,

$$\begin{aligned}
E_n^{(1)} &= \langle n, j, m_j, \ell, s|U|n, j, m_j, \ell, s\rangle \\
&= \frac{g_e e^2}{(2m_e c)^2}\frac{\hbar^2}{2}\Big(j(j+1) - s(s+1) - \ell(\ell+1)\Big)\Big\langle\frac{1}{r^3}\Big\rangle \\
&= \frac{g_e e^2}{(2m_e c)^2}\frac{\hbar^2}{2}\Big(j(j+1) - s(s+1) - \ell(\ell+1)\Big)\frac{1}{a_0^3 n^3 \ell(\ell+\frac{1}{2})(\ell+1)} \\
(g_e \approx 2) &= \frac{e^2\hbar^2}{4(m_e c)^2}\Big(\frac{m_e e^2}{\hbar^2}\Big)^3\frac{1}{n^3}\frac{j(j+1) - \frac{3}{4} - \ell(\ell+1)}{\ell(\ell+\frac{1}{2})(\ell+1)} \\
&= \frac{(e^2)^4}{4(\hbar c)^4}\frac{m_e c^2}{n^3}\frac{j(j+1) - \frac{3}{4} - \ell(\ell+1)}{\ell(\ell+\frac{1}{2})(\ell+1)} \\
&= E_n^{(0)}\frac{\alpha^2}{n^2}\frac{n[\frac{3}{4} + \ell(\ell+1) - j(j+1)]}{2\ell(\ell+\frac{1}{2})(\ell+1)}
\end{aligned}$$

where $E_n^{(0)} = -\frac{1}{2}\alpha^2\frac{m_e c^2}{n^2}$, $\alpha = \frac{e^2}{\hbar c}$.