Final

1. Zeeman effect

The sodium D-lines are the transitions of $3\, p_{3/2} \rightarrow 3\, s_{1/2}$ (5890 Å) and $3\, p_{1/2} \rightarrow 3\, s_{1/2}$ (5896 Å). The corresponding photon energies are 2.105 eV and 2.103 eV, respectively.

In a weak magnetic field, the $3\, p_{3/2}$ level splits into four levels with $m_j = \frac{1}{2}, \frac{3}{2}, \frac{1}{2}, \frac{3}{2}$, the $3\, p_{1/2}$ level into two levels with $m_j = \frac{1}{2}, -\frac{1}{2}$, and the $3\, s_{1/2}$ level into two levels with $m_j = \frac{1}{2}, -\frac{1}{2}$. Following Sakurai Eq. (5.3.32), the energy shifts are (in the Gaussian unit)

$$\Delta E_B = -\frac{\epsilon_B}{2mc} m_j (1 \pm \frac{1}{2}l_fT)$$

which are

$$\Delta E_B = -\frac{\epsilon_B}{2mc} \frac{1}{2} m_j \text{ for } 3\, p_{3/2},$$
$$\Delta E_B = -\frac{\epsilon_B}{2mc} \frac{3}{2} m_j \text{ for } 3\, p_{1/2},$$
$$\Delta E_B = -\frac{\epsilon_B}{2mc} 2 m_j \text{ for } 3\, s_{1/2}.$$

The Bohr magneton is $\frac{\epsilon_B}{2mc} = -5.788 \times 10^{-5}$ eV / T.

Under the electric dipole transitions, we have the selection rules that $\Delta l = \pm 1$, and $\Delta m_j = 0, \pm 1$. Therefore the allowed transitions, $m_j$, and the photon energies are:

$$3\, p_{3/2} \rightarrow 3\, s_{1/2}$$
$$\frac{1}{2} \rightarrow \frac{1}{2}: E = 2.105 \text{ eV} - \frac{\epsilon_B}{2mc} \left(\frac{1}{2} \frac{1}{2} - 2 \frac{1}{2}\right) eV / T = (2.105 - 5.788 \times 10^{-5} B / T)eV$$
$$\frac{1}{2} \rightarrow \frac{3}{2}: E = 2.105 \text{ eV} - \frac{\epsilon_B}{2mc} \left(\frac{1}{2} \frac{3}{2} - 2 \frac{1}{2}\right) eV / T = (2.105 - 1.929 \times 10^{-5} B / T)eV$$
$$\frac{1}{2} \rightarrow -\frac{1}{2}: E = 2.105 \text{ eV} - \frac{\epsilon_B}{2mc} \left(\frac{1}{2} \frac{1}{2} - 2 \frac{1}{2}\right) eV / T = (2.105 + 5.788 \times 10^{-5} B / T)eV$$
$$\frac{1}{2} \rightarrow -\frac{3}{2}: E = 2.105 \text{ eV} - \frac{\epsilon_B}{2mc} \left(\frac{1}{2} \frac{3}{2} - 2 \frac{3}{2}\right) eV / T = (2.105 + 1.929 \times 10^{-5} B / T)eV$$

$$3\, p_{1/2} \rightarrow 3\, s_{1/2}$$
$$\frac{1}{2} \rightarrow \frac{1}{2}: E = 2.103 \text{ eV} - \frac{\epsilon_B}{2mc} \left(\frac{1}{2} \frac{1}{2} - 2 \frac{1}{2}\right) eV / T = (2.103 - 3.859 \times 10^{-5} B / T)eV$$
$$\frac{1}{2} \rightarrow -\frac{1}{2}: E = 2.103 \text{ eV} - \frac{\epsilon_B}{2mc} \left(\frac{1}{2} \frac{1}{2} - 2 \frac{1}{2}\right) eV / T = (2.103 + 7.717 \times 10^{-5} B / T)eV$$
$$\frac{1}{2} \rightarrow \frac{3}{2}: E = 2.103 \text{ eV} - \frac{\epsilon_B}{2mc} \left(\frac{1}{2} \frac{3}{2} - 2 \frac{3}{2}\right) eV / T = (2.103 - 7.717 \times 10^{-5} B / T)eV$$
$$\frac{1}{2} \rightarrow -\frac{3}{2}: E = 2.103 \text{ eV} - \frac{\epsilon_B}{2mc} \left(\frac{1}{2} \frac{3}{2} - 2 \frac{3}{2}\right) eV / T = (2.103 + 3.859 \times 10^{-5} B / T)eV$$

The 5890 Å line splits into six equally spaced lines, while the 5896 Å splits into four lines with unequal spacings.
The fact that there are even number of lines with unequal splittings was called "anomalous Zeeman effect" because it could not be "explained" by semi-classical expectations without the spin.

By the way, for the magnetic field larger than a few Tesla, obviously the \(2p_{1/2}\) and \(2p_{3/2}\) states come close and hence the magnetic field cannot be treated "weak." Both Paschen-Back and Zeeman effects need to be considered simultaneously using the degenerate perturbation theory by diagonalizing the perturbation matrix as we discussed in the class.

2. Ion in a crystal field

(a)

The Coulomb potential due to the positive ions on the electron is

\[
e^2 \left( \frac{1}{\sqrt{(x-a)^2+y^2+z^2}} + \frac{1}{\sqrt{(x+a)^2+y^2+z^2}} + \frac{1}{\sqrt{x^2+(y-a)^2+z^2}} + \frac{1}{\sqrt{x^2+(y+a)^2+z^2}} \right).
\]

Taylor expanding it to the second order,

\[
\text{Simplify}[\text{Series}[
\frac{e^2}{\sqrt{(x-a)^2+y^2+z^2}} + \frac{1}{\sqrt{(x+a)^2+y^2+z^2}} + \frac{1}{\sqrt{x^2+(y-a)^2+z^2}} + \frac{1}{\sqrt{x^2+(y+a)^2+z^2}}
\],
\{x \rightarrow tx, y \rightarrow ty, z \rightarrow tz\}, \{t, 0, 2\}]\]

\[
\frac{4e^2}{\sqrt{a^2}} + \frac{e^2}{(a^2)^{3/2}} \left( \frac{x^2+y^2-2z^2}{(a^2)^{3/2}} \right) t + O[t^3]
\]

The potential is therefore

\[
V = \frac{4e^2}{a} + \frac{e^2}{a^{3/2}} (x^2+y^2-2z^2)
\]
(b)

The second term $\Delta V = \frac{e}{4\pi r} (x^2 + y^2 - 2z^2)$ is the perturbation on the $p$-electron. Note that its form is that of the quadrupole moment, and hence is a spherical tensor of $q = 2$ and $k = 0$. Therefore the expectation values are proportional to the Clebsch-Gordan coefficients

$$
\begin{align*}
\text{Table[ClebschGordan]} \{\{1, 1\}, \{2, 0\}, \{1, 1\}, \{1, -1, 1\}\}
\end{align*}
$$

It is clear that the energy levels are split into a degenerate doublet ($m = \pm 1$) and a separate singlet ($m = 0$).

To compute the actual expectation values, we use $\psi = R(r) Y_l^m$,

$$
r^2 Y_2^0 = \sqrt{\frac{5}{16\pi}} r^2 (3 \cos^2 \theta - 1) = -\sqrt{\frac{5}{16\pi}} (x^2 + y^2 - 2z^2). \quad \text{Then}
$$

$$
\langle l, m | x^2 + y^2 - 2z^2 | l, m \rangle = \int r^2 d r d \Omega R^2(r) Y_l^m(x^2 + y^2 - 2z^2) Y_l^m
$$

$$
= -\sqrt{\frac{16\pi}{5}} \int r^4 d r d \Omega \int r^2 d \Omega R^2(r) Y_l^{m_1} Y_2^0 Y_l^m
$$

$$
= -\sqrt{\frac{16\pi}{5}} \langle r^2 \rangle \int d \Omega Y_l^{m_1} Y_2^0 Y_l^m
$$

Now the last factor can be simplified using Sakurai’s Eq. (3.7.73)

$$
\int d \Omega Y_l^{m_1} Y_2^0 Y_l^m = \sqrt{\frac{5}{4\pi}} \langle l, 2; 00 \mid l, 10 \rangle \langle l, 2; m0 \mid l, m \rangle
$$

For our case, $l = 1$, and hence

$$
\int d \Omega Y_1^{m_1} Y_2^0 Y_1^m = \sqrt{\frac{5}{4\pi}} \langle l, 2; 00 \mid l, 10 \rangle \langle l, 2; m0 \mid l, m \rangle
$$

Finally we obtain

$$
\langle l, m | x^2 + y^2 - 2z^2 | l, m \rangle = \langle l, 2; 00 \mid l, 10 \rangle \langle l, 2; m0 \mid l, m \rangle
$$

$$
= \langle r^2 \rangle \langle l, 2; 00 \mid l, 10 \rangle \langle l, 2; m0 \mid l, m \rangle
$$

$$
= \langle r^2 \rangle \langle \frac{4}{5}, \frac{4}{5} \mid \frac{2}{5}, \frac{2}{5} \rangle
$$

The energy shifts are

$$
\frac{e^2}{4\pi} \langle 1, m \mid x^2 + y^2 - 2z^2 \mid 1, m \rangle = \frac{2e^2}{3\alpha^2} \langle r^2 \rangle (1, -2, 1)
$$

The degeneracy is due to the time-reversal invariance of the Hamiltonian, which interchanges $m = 1$ and $m = -1$. Another symmetry that explains the degeneracy is the 180 degrees rotation around $x$ or $y$ axis, which also interchanges $m = 1$ and $m = -1$ states. Either of them leaves the Hamiltonian invariant and hence guarantees the degeneracy.

3. Tritium Beta Decay

This is a problem where the hydrogen nucleus "suddenly" changes its charge from $Z = 1$ to $Z = 2$. The needed wave functions are

$$
R_{1s} = a^{-3/2} 2 e^{-r/a}
$$

$$
\frac{2 e^{-r/2}}{a^{3/2}}
$$
\[ R_{2s} = (2a)^{-3/2} \left( 2 - \frac{r}{a} \right) e^{-r/(2a)} \]

\[ \frac{e^{-r/(2a)} (2 - \frac{r}{a})}{2 \sqrt{2} a^{1/2}} \]

\[ R_{2p} = (2a)^{-3/2} \frac{r}{\sqrt{3} a} e^{-r/(2a)} \]

\[ \frac{e^{-r/(2a)} r}{2 \sqrt{6} a^{5/2}} \]

Just before the beta decay, the electron was in the 1s state with \( Z = 1 \). Note that the Bohr radius changes to
\[ a \to \frac{a}{Z} = \frac{a}{2} \] after the beta decay. Therefore the probability to find the electron in the 1s state of the He\(^+\) ion is given by the overlap integral,

\[ \int_{r} R_{1s} r^2, \{ r, 0, \infty \}, \text{Assumptions} \to a > 0 \]

\[ \frac{16 \sqrt{2}}{27} \]

\[ N[\%^2] \]

0.702332

Hence 70.2%. The probability to find the electron in the 2s state of the He\(^+\) ion is

\[ \int_{r} R_{2s} r^2, \{ r, 0, \infty \}, \text{Assumptions} \to a > 0 \]

\[ \frac{1}{2} \]

\[ N[\%^2] \]

0.25

Hence 25.0%.

Finally, the 2p state has \( l = 1 \), while the sudden change in the nuclear charge does not change the spherical symmetry, and hence the probability to find the electron in the 2p state, or any states with non-zero \( l \), is zero. (Of course this part of the conclusion depends crucially on the assumption to ignore the nuclear recoil.)
4. Dyson Series

(a)

The Dyson series up to $O(V^2)$ is

$$U_i(t) = 1 + \frac{-i}{\hbar} \int_0^t V_i(t') \, dt' + \left( \frac{-i}{\hbar} \right)^2 \int_0^t \int_0^{t'} V_i(t') \, V_j(t'') \, dt'' \, dt' + O(V^3).$$

We take its matrix element between the same states,

$$\langle i | U_i(t) | i \rangle = 1 + \frac{-i}{\hbar} \int_0^t \langle i | V_i(t') | i \rangle \, dt' + \left( \frac{-i}{\hbar} \right)^2 \int_0^t \int_0^{t'} \langle i | V_i(t') \, V_j(t'') | i \rangle \, dt'' \, dt' + O(V^3)$$

The second term is

$$\frac{-i}{\hbar} \int_0^t e^{iE_i t' / \hbar} V_i e^{-iE_i t' / \hbar} \, dt' = \frac{-i}{\hbar} V_{ii} \, t,$

which is identified with the term $\frac{-i}{\hbar} \Delta_{ii}^{(1)} \, t$ in Eq. (1). Therefore we reproduce the result from the time-independent perturbation theory

$$\Delta_{ii}^{(1)} = V_{ii}.$$

The third term produces many interesting contributions. Inserting the complete set of intermediate states,

$$\left( \frac{-i}{\hbar} \right)^2 \int_0^t \int_0^{t'} \langle i | V_i(t') \, V_j(t'') | i \rangle \, dt'' \, dt' = \frac{-i}{\hbar} \int_0^t \int_0^{t'} \sum_{m} \langle i | V_i(t') | m \rangle \langle m | V_j(t'') | i \rangle \, dt'' \, dt'$$

$$= \frac{-i}{\hbar} \int_0^t \int_0^{t'} \sum_{m} V_{im} e^{-i(E_{m} - E_{i}) t' / \hbar} V_{mj} e^{i(E_{m} - E_{j}) t'' / \hbar} \, dt'' \, dt'$$

$$= \frac{-i}{\hbar} \int_0^t \int_0^{t'} \left( V_{ji} \, t' + \sum_{m \neq i} V_{im} \right) \sum_{m} \frac{1}{E_{m} - E_{i}} \left( t - \frac{e^{i(E_{m} - E_{i}) t'' / \hbar} - 1}{E_{m} - E_{i}} \right)$$

$$= \frac{-i}{\hbar} \int_0^t \int_0^{t'} \left( V_{ji} \, t' + \sum_{m \neq i} V_{im} \right) \sum_{m} \frac{1}{E_{m} - E_{i}} \left( t - \frac{e^{i(E_{m} - E_{i}) t'' / \hbar} - 1}{E_{m} - E_{i}} \right)$$

$$= \frac{-i}{\hbar} \int_0^t \int_0^{t'} \left( \sum_{m \neq i} \frac{|W_{im}|^2}{E_{m} - E_{i}} \right) \sum_{m} \frac{1}{E_{m} - E_{i}} \left( t - \frac{e^{i(E_{m} - E_{i}) t'' / \hbar} - 1}{E_{m} - E_{i}} \right)$$

The first term is $\frac{1}{\hbar} \Delta_{ii}^{(1)} \, t^2$, while the second term is $\frac{-i}{\hbar} \Delta_{ii}^{(2)} \, t$ with $\Delta_{ii}^{(2)} = \sum_{m \neq i} \frac{|W_{im}|^2}{E_{m} - E_{i}}$.

The last term is a part of the wave function renormalization factor

$$Z_i = 1 - \sum_{m \neq i} \frac{|W_{im}|^2}{E_{m} - E_{i}}.$$

Finally, the third term is the time-evolution of the state $m$ mixed to the state $i$ due to the perturbation by $\frac{V_{im}}{E_{i} - E_{m}}$. For $t \to \infty$, this term oscillates rapidly and can be dropped; however it is there for a finite $t$.

Just in case you are wondering why this works, here is the reason (not a part of the exam). Using the notation of the time-independent perturbation theory, our initial and the final states are the unperturbed $\ket{\phi^{(0)}}$. It can be expanded in the true Hamiltonian eigenstates as

$$\ket{\phi^{(0)}} = \sum_{m} \langle m | \phi^{(0)} \rangle \ket{m} + \sum_{m \neq i} |i \rangle \langle i | \phi^{(0)} \rangle + \sum_{m \neq i} |m \rangle \langle m | \phi^{(0)} \rangle.$$

The wave function renormalization factor is

$$Z_i = |\langle i | \phi^{(0)} \rangle|^2,$$

and hence (with a proper phase convention)

$$\ket{\phi^{(0)}} = Z_i^{1/2} \ket{i} + \sum_{m} \ket{m} \ket{m | \phi^{(0)} \rangle}.$$

The time-evolution operator in the interaction picture is $U_i(t) = e^{iH_0 t / \hbar} \, U(t)$ (Eq. (5.6.9) in Sakurai with $t_0 = 0$), and hence

$$\langle \phi^{(0)} | U_i(t) | \phi^{(0)} \rangle = \langle \phi^{(0)} | e^{iH_0 t / \hbar} \, U(t) | \phi^{(0)} \rangle = e^{iE_i t / \hbar} \langle \phi^{(0)} | U(t) | \phi^{(0)} \rangle$$

$$= e^{iE_i t / \hbar} (Z_i \ket{i} \bra{i} + \sum_{m \neq i} \bra{m} \bra{m} \ket{m} \ket{m | \phi^{(0)} \rangle \rangle}$$

$$= Z_i e^{-i(E_i - E_m) t / \hbar} + \sum_{m \neq i} e^{-i(E_i - E_m) t / \hbar} \left( \bra{m} \ket{\phi^{(0)}} \right)^2.$$
(b)

Following the same steps as above,

\[
\left(\frac{2}{\hbar} \right)^2 \int_0^T \int_0^T \langle \bar{i} | V(t') V(t) | \bar{i} \rangle \, dt' \, dt = \frac{1}{\hbar^2} \int_0^T \int_0^T \sum_m \langle \bar{i} | V(t') | m \rangle \langle m | V(t) | \bar{i} \rangle \, dt' \, dt
\]

\[
= \frac{1}{\hbar^2} \int_0^T \sum_m V_m \cos \omega t' e^{-i(E_m-E_\bar{i})t'/\hbar} V_{m'j} \cos \omega t'' e^{-i(E_m-E_{\bar{j}})t''/\hbar} \, dt' \, dt''
\]

\[
= \frac{1}{\hbar^2} \int_0^T \sum_m V_{m'j}^2 \cos \omega t' \cos \omega t'' + \sum_{m'j} V_m \cos \omega t' e^{-i(E_m-E_\bar{i})t'/\hbar} V_{m'j} \cos \omega t'' e^{-i(E_m-E_{\bar{j}})t''/\hbar} \, dt' \, dt''
\]

Because we are interested in the term that grows as \( t \), we can drop all the other terms. Namely, the integrand of the first term oscillates rapidly for large \( t \) and \( t' \), and we drop it. The second term is

\[
= \frac{1}{\hbar^2} \sum_{m'j} V_{m'j} \int_0^T \cos \omega t' e^{-i(E_m-E_\bar{i})t'/\hbar} \left( \frac{e^{-i(E_m-E_{\bar{j}})t''/\hbar}}{-(E_m-E_{\bar{j}})h/\hbar} + \frac{e^{-i(E_m-E_{\bar{j}})t''/\hbar}}{-(E_m-E_{\bar{j}})h/\hbar} \right) \, dt''
\]

The terms with \( e^{-i(E_m-E_{\bar{j}})t''/\hbar} \) oscillate rapidly and can be dropped. Then,

\[
= \frac{1}{\hbar^2} \sum_{m'j} V_{m'j} \int_0^T \frac{1}{4} (e^{i\omega t'} + e^{-i\omega t'}) \left( \frac{e^{-i(E_m-E_{\bar{j}})t''/\hbar}}{-(E_m-E_{\bar{j}})h/\hbar} + \frac{e^{-i(E_m-E_{\bar{j}})t''/\hbar}}{-(E_m-E_{\bar{j}})h/\hbar} \right) \, dt''
\]

Only the terms without the oscillatory factors give \( O(\hbar) \) contributions,

\[
= \frac{1}{\hbar} \sum_{m'j} V_{m'j} \int_0^T \frac{1}{4} \left( \frac{1}{(E_m-E_{\bar{i}}+\hbar/\omega)} + \frac{1}{(E_m-E_{\bar{i}}-\hbar/\omega)} \right) \, dt''
\]

\[
= \frac{1}{\hbar} \sum_{m'j} V_{m'j} \int_0^T \frac{2}{4} \frac{(E_m-E_{\bar{j})}}{(E_m-E_{\bar{j}}+\hbar/\omega)(E_m-E_{\bar{j}}-\hbar/\omega)} \, dt''
\]

\[
= \frac{1}{\hbar} \frac{1}{2} \sum_{m'j} \frac{|V_{m'j}|^2 (E_m-E_{\bar{j})}}{(E_m-E_{\bar{j}}+\hbar/\omega)(E_m-E_{\bar{j}}-\hbar/\omega)}
\]

Therefore,

\[
\Delta_{(2)}^{(2)} = \frac{1}{\hbar} \sum_{m'j} \frac{|V_{m'j}|^2 (E_m-E_{\bar{j})}}{(E_m-E_{\bar{j}}+\hbar/\omega)(E_m-E_{\bar{j}}-\hbar/\omega)}
\]

The expression does not go back to that in the time-independent perturbation theory in the limit \( \omega \to 0 \). This is because the quantity is the time average of the oscillating function \( \langle \cos^2 \omega t \rangle = \frac{1}{2} \).

(c)

In this case, the perturbation is \( V = e E_0 z \cos(k x - \omega t) \) and hence

\[
\Delta_{(2)} = \frac{1}{2} e^2 E_0^2 \sum_{m'j} \frac{|V_{m'j}|^2 (E_m-E_{\bar{j})}}{(E_m-E_{\bar{j}}+\hbar/\omega)(E_m-E_{\bar{j}}-\hbar/\omega)}.
\]

Here, we used the electric dipole approximation and set \( k x = 0 \).

This energy shift should be compared to the energy of the electromagnetic wave

\[
\int d^3 x \frac{1}{2} (E_0 \cos(k x - \omega t))^2 = \int d^3 x \frac{1}{2} E_0^2, \text{ where the time average } \langle \cos^2 \omega t \rangle = \frac{1}{2} \text{ is taken. Therefore, it corrects the Lagrangian density as}
\]

\[
\frac{1}{4} E_0^2 \to \frac{1}{4} E_0^2 \left( 1 - \frac{N}{\alpha} \right) \frac{2 e^2}{2} \sum_{m'j} \frac{|V_{m'j}|^2 (E_m-E_{\bar{j})}}{(E_m-E_{\bar{j}}+\hbar/\omega)(E_m-E_{\bar{j}}-\hbar/\omega)}
\]

where \( \frac{N}{\alpha} \) is the number density of the hydrogen atom, and hence the polarizability is

\[
\alpha = 2 e^2 E_0^2 \sum_{m'j} \frac{|V_{m'j}|^2 (E_m-E_{\bar{j})}}{(E_m-E_{\bar{j}}+\hbar/\omega)(E_m-E_{\bar{j}}-\hbar/\omega)}
\]

which agrees with the static case when \( \omega \to 0 \).
With the polarizability and the number density $n$,

$$n(\omega) = (1 + \frac{N}{V} \alpha)^{1/2} = 1 + \frac{N}{V} 2 e^2 E_0^2 \sum_{m} \lfloor \frac{E_m - E_i}{(E_i - E_m)^2 - (\hbar \omega)^2} \rfloor.$$

Clearly the denominator is smaller for larger $\hbar \omega < |E_i - E_m|$, and hence the index of refraction increases for the shorter wavelength. This leads to the prediction that red is at the top and violet at the bottom in a rainbow, which obviously explains the our experience. See, e.g., http://acept.la.asu.edu/PiN/mod/light/opticsnature/rainbows.html

Now you can proudly tell your parents that you fully understand the rainbow from the first principle.