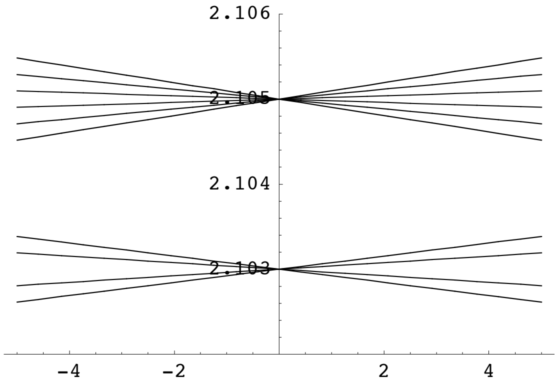
# Final

## 1. Zeeman effect

The sodium D-lines are the transitions of $3\,p_{3/2} \to 3\,s_{1/2}$ (5890 Å) and $3\,p_{1/2} \to 3\,s_{1/2}$ (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 $m_j = \frac{3}{2}, \frac{1}{2}, \frac{-1}{2}, \frac{-3}{2}$, 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 leves with $m_j = \frac{1}{2}, \frac{-1}{2}$. Following Sakurai Eq. (5.3.32), the energy shifts are (in the Gaussian unit)
$\Delta E_B = -\frac{e\hbar B}{2mc}\, m_j(1 \pm \frac{1}{2l+1})$
which are
$\Delta E_B = -\frac{e\hbar B}{2mc}\,\frac{4}{3}\, m_j$ for $3\,p_{3/2}$,
$\Delta E_B = -\frac{e\hbar B}{2mc}\,\frac{2}{3}\, m_j$ for $3\,p_{1/2}$,
$\Delta E_B = -\frac{e\hbar B}{2mc}\, 2\, m_j$ for $3\,s_{1/2}$.
The Bohr magneton is $\frac{e\hbar}{2mc} = -5.788\; 10^{-5}\ \mathrm{eV}/T$.

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:
$3\,p_{3/2} \to 3\,s_{1/2}$
$\frac{3}{2} \to \frac{1}{2}: E = 2.105\ \mathrm{eV} - \frac{e\hbar B}{2mc}\,(\frac{4}{3}\,\frac{3}{2} - 2\,\frac{1}{2})\ \mathrm{eV}/T = (2.105 + 5.788\; 10^{-5}\ B/T)\ \mathrm{eV}$
$\frac{1}{2} \to \frac{1}{2}: E = 2.105\ \mathrm{eV} - \frac{e\hbar B}{2mc}\,(\frac{4}{3}\,\frac{1}{2} - 2\,\frac{1}{2})\ \mathrm{eV}/T = (2.105 - 1.929\; 10^{-5}\ B/T)\ \mathrm{eV}$
$\frac{1}{2} \to \frac{-1}{2}: E = 2.105\ \mathrm{eV} - \frac{e\hbar B}{2mc}\,(\frac{4}{3}\,\frac{1}{2} - 2\,\frac{-1}{2})\ \mathrm{eV}/T = (2.105 + 9.647\; 10^{-5}\ B/T)\ \mathrm{eV}$
$\frac{-1}{2} \to \frac{1}{2}: E = 2.105\ \mathrm{eV} - \frac{e\hbar B}{2mc}\,(\frac{4}{3}\,\frac{-1}{2} - 2\,\frac{1}{2})\ \mathrm{eV}/T = (2.105 - 9.647\; 10^{-5}\ B/T)\ \mathrm{eV}$
$\frac{-1}{2} \to \frac{-1}{2}: E = 2.105\ \mathrm{eV} - \frac{e\hbar B}{2mc}\,(\frac{4}{3}\,\frac{1}{2} - 2\,\frac{1}{2})\ \mathrm{eV}/T = (2.105 + 1.929\; 10^{-5}\ B/T)\ \mathrm{eV}$
$\frac{-3}{2} \to \frac{-1}{2}: E = 2.105\ \mathrm{eV} - \frac{e\hbar B}{2mc}\,(\frac{4}{3}\,\frac{-3}{2} - 2\,\frac{-1}{2})\ \mathrm{eV}/T = (2.105 - 5.78810^{-5}\ B/T)\ \mathrm{eV}$
$3\,p_{1/2} \to 3\,s_{1/2}$
$\frac{1}{2} \to \frac{1}{2}: E = 2.103\ \mathrm{eV} - \frac{e\hbar B}{2mc}\,(\frac{4}{3}\,\frac{3}{2} - 2\,\frac{1}{2})\ \mathrm{eV}/T = (2.103 - 3.859\; 10^{-5}\ B/T)\ \mathrm{eV}$
$\frac{1}{2} \to \frac{-1}{2}: E = 2.103\ \mathrm{eV} - \frac{e\hbar B}{2mc}\,(\frac{4}{3}\,\frac{3}{2} - 2\,\frac{-1}{2})\ \mathrm{eV}/T = (2.103 + 7.717\; 10^{-5}\ B/T)\ \mathrm{eV}$
$\frac{-1}{2} \to \frac{1}{2}: E = 2.103\ \mathrm{eV} - \frac{e\hbar B}{2mc}\,(\frac{4}{3}\,\frac{3}{2} - 2\,\frac{1}{2})\ \mathrm{eV}/T = (2.103 - 7.717\; 10^{-5}\ B/T)\ \mathrm{eV}$
$\frac{-1}{2} \to \frac{-1}{2}: E = 2.103\ \mathrm{eV} - \frac{e\hbar B}{2mc}\,(\frac{4}{3}\,\frac{3}{2} - 2\,\frac{1}{2})\ \mathrm{eV}/T = (2.103 + 3.859\; 10^{-5}\ B/T)\ \mathrm{eV}$
The 5890 Å line splits into six equally spaced lines, while the 5896 Å splits into four lines with unequal spacings.

```
In[22]:= Plot[{2.105 + 5.788 10^-5 B, 2.105 - 1.929 10^-5 B, 2.105 + 9.647 10^-5 B, 2.105 - 9.647 10^-5 B,
    2.105 + 1.929 10^-5 B, 2.105 - 5.788 10^-5 B, 2.103 - 3.859 10^-5 B, 2.103 + 7.717 10^-5 B,
    2.103 - 7.717 10^-5 B, 2.103 + 3.859 10^-5 B}, {B, -5, 5}, PlotRange → {2.102, 2.106}]
```




```
Out[22]= - Graphics -
```

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 $2\,p_{1/2}$ and $2\,p_{3/2}$ 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,

$$\text{Simplify}\Big[\text{Series}\Big[e^2\left(\frac{1}{\sqrt{(x-a)^2+y^2+z^2}}+\frac{1}{\sqrt{(x+a)^2+y^2+z^2}}+\frac{1}{\sqrt{x^2+(y-a)^2+z^2}}+\frac{1}{\sqrt{x^2+(y+a)^2+z^2}}\right)\text{/.}\ \{x\to t\,x,\ y\to t\,y,\ z\to t\,z\},\ \{t,0,2\}\Big]\Big]$$

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

The potential is therefore
$V = 4\,\frac{e^2}{a}+\frac{e^2}{a^3}\,(x^2+y^2-2\,z^2)$

## (b)

The second term $\Delta V = \frac{e^2}{a^3}(x^2 + y^2 - 2z^2)$ 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

```
Table[ClebschGordan[{1, l}, {2, 0}, {1, l}], {l, -1, 1}]
```

$$\left\{\frac{1}{\sqrt{10}}, -\sqrt{\frac{2}{5}}, \frac{1}{\sqrt{10}}\right\}$$

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

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

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

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

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

$\int d\,\Omega\; Y_l^{m*}\, Y_2^0\, Y_l^m = \sqrt{\frac{5}{4\pi}}\, \langle l, 2; 0\,0 \,|\, l\,2; l\,0\rangle \langle l, 2; m\,0 \,|\, l\,2; l\,m\rangle$

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

$\int d\,\Omega\; Y_1^{m*}\, Y_2^0\, Y_1^m = \sqrt{\frac{5}{4\pi}} \left(-\sqrt{\frac{2}{5}}\right)\left(\frac{1}{\sqrt{10}}, -\sqrt{\frac{2}{5}}, \frac{1}{\sqrt{10}}\right) = \sqrt{\frac{5}{4\pi}}\,(-\frac{1}{5}, \frac{2}{5}, -\frac{1}{5})$.

Finally we obtain

$\langle l, m \,|\, x^2 + y^2 - 2z^2 \,|\, l, m\rangle = -\sqrt{\frac{16\pi}{5}}\, \langle r^2\rangle \sqrt{\frac{5}{4\pi}}\,(-\frac{1}{5}, \frac{2}{5}, -\frac{1}{5})$

$= \langle r^2\rangle (\frac{2}{5}, -\frac{4}{5}, \frac{2}{5})$.

The energy shifts are

$\frac{e^2}{a^3}\, \langle 1, m \,|\, x^2 + y^2 - 2z^2 \,|\, 1, m\rangle = \frac{2e^2}{5a^2}\, \langle r^2\rangle (1, -2, 1)$.

The degeneracy is due to the time-reversal invariance of the Hamitonian, 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_{1 s} = a^{-3/2} 2 E^{-r/a}
```

$$\frac{2\, e^{-\frac{r}{a}}}{a^{3/2}}$$

```
R2 s = (2 a)^-3/2 (2 - r/a) E^-r/(2 a)
```

$$\frac{e^{-\frac{r}{2a}}\left(2-\frac{r}{a}\right)}{2\sqrt{2}\,a^{3/2}}$$

```
R2 p = (2 a)^-3/2 r/(√3 a) E^-r/(2 a)
```

$$\frac{e^{-\frac{r}{2a}}\,r}{2\sqrt{6}\,a^{5/2}}$$

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,

```
R1 s /. {a → a/2}
```

$$\frac{4\sqrt{2}\,e^{-\frac{2r}{a}}}{a^{3/2}}$$

```
Integrate[% R1 s r^2, {r, 0, ∞}, Assumptions → 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

```
R2 s /. {a → a/2}
```

$$\frac{e^{-\frac{r}{a}}\left(2-\frac{2r}{a}\right)}{a^{3/2}}$$

```
Integrate[% R1 s r^2, {r, 0, ∞}, Assumptions → 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
$U_I(t) = 1 + \frac{-i}{\hbar} \int_0^t V_I(t')\, d t' + (\frac{-i}{\hbar})^2 \int_0^t \int_0^{t'} V_I(t')\, V_I(t'')\, d t''\, d t' + O(V^3)$.
We take its matrix element between the same states,
$\langle i \mid U_I(t) \mid i \rangle = 1 + \frac{-i}{\hbar} \int_0^t \langle i \mid V_I(t') \mid i \rangle\, d t' + (\frac{-i}{\hbar})^2 \int_0^t \int_0^{t'} \langle i \mid V_I(t')\, V_I(t'') \mid i \rangle\, d t''\, d t' + O(V^3)$
The second term is
$\frac{-i}{\hbar} \int_0^t e^{i E_i t'/\hbar}\, V_{i\,i}\, e^{-i E_i t'/\hbar}\, d t' = \frac{-i}{\hbar}\, V_{i\,i}\, t$,
which is identified with the term $\frac{-i}{\hbar}\, \Delta_i^{(1)}\, t$ in Eq. (1). Therefore we reproduce the result from the time-independent perturbation theory
$\Delta_i^{(1)} = V_{i\,i}$.
The third term produces many interesting contributions. Inserting the complete set of intermediate states,
$(\frac{-i}{\hbar})^2 \int_0^t \int_0^{t'} \langle i \mid V_I(t')\, V_I(t'') \mid i \rangle\, d t''\, d t' = \frac{-1}{\hbar^2} \int_0^t \int_0^{t'} \sum_m \langle i \mid V_I(t') \mid m \rangle \langle m \mid V_I(t'') \mid i \rangle\, d t''\, d t'$
$= \frac{-1}{\hbar^2} \int_0^t \int_0^{t'} \sum_m V_{i\,m}\, e^{-i(E_m - E_i)\, t'/\hbar}\, V_{m\,i}\, e^{i(E_i - E_m)\, t''/\hbar}\, d t''\, d t'$
$= \frac{-1}{\hbar^2} \int_0^t \int_0^{t'} (V_{i\,i}\, V_{i\,i} + \sum_{m \neq i} V_{i\,m}\, e^{-i(E_m - E_i)\, t'/\hbar}\, V_{m\,i}\, e^{-i(E_i - E_m)\, t''/\hbar})\, d t''\, d t'$
$= \frac{-1}{\hbar^2} \left(\frac{1}{2}\, V_{i\,i}{}^2\, t^2 + \sum_{m \neq i} \left| V_{i\,m} \right|^2 \int_0^t \int_0^{t'} e^{-i(E_m - E_i)\, (t' - t'')/\hbar}\, d t''\, d t'\right)$
$= \frac{-1}{\hbar^2} \left(\frac{1}{2}\, V_{i\,i}{}^2\, t^2 + \sum_{m \neq i} \left| V_{i\,m} \right|^2 \int_0^t \frac{1 - e^{-i(E_m - E_i)\, t'/\hbar}}{i(E_m - E_i)/\hbar}\, d t'\right)$
$= \frac{-1}{\hbar^2} \left(\frac{1}{2}\, V_{i\,i}{}^2\, t^2 + \sum_{m \neq i} \left| V_{i\,m} \right|^2 \frac{1}{i(E_m - E_i)/\hbar} \left(t - \frac{e^{-i(E_m - E_i)\, t/\hbar} - 1}{-i(E_m - E_i)/\hbar}\right)\right)$
$= \frac{1}{2}\, \frac{-1}{\hbar^2}\, V_{i\,i}{}^2\, t^2 + \sum_{m \neq i} \left| V_{i\,m} \right|^2 \frac{1}{E_i - E_m} \left(\frac{-i}{\hbar}\, t + \frac{e^{-i(E_m - E_i)\, t/\hbar} - 1}{E_i - E_m}\right)$
$= \frac{1}{2}\, \frac{-1}{\hbar^2}\, V_{i\,i}{}^2\, t^2 + \frac{-i}{\hbar} \left(\sum_{m \neq i} \frac{|V_{i\,m}|^2}{E_i - E_m}\, t\right) + \left(\sum_{m \neq i} \frac{|V_{i\,m}|^2}{(E_i - E_m)^2}\, e^{-i(E_m - E_i)\, t/\hbar}\right) - \left(\sum_{m \neq i} \frac{|V_{i\,m}|^2}{(E_i - E_m)^2}\right)$
The first term is $\frac{1}{2!}\, (\frac{-i}{\hbar}\, \Delta_i^{(1)}\, t)^2$, while the second term is $\frac{-i}{\hbar}\, \Delta_i^{(2)}\, t$ with
$\Delta_i^{(2)} = \sum_{m \neq i} \frac{|V_{i\,m}|^2}{E_i - E_m}$.
The last term is a part of the wave function renormalization factor
$Z_i = 1 - \sum_{m \neq i} \frac{|V_{i\,m}|^2}{(E_i - E_m)^2}$.
Finally, the third term is the time-evolution of the state $m$ mixed to the state $i$ due to the perturbation by $\frac{V_{i\,m}}{E_i - E_m}$. 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 intial and the final states are the unperturbed $\mid i^{(0)} \rangle$. It can be expanded in the true Hamiltonian eigenstates as
$\mid i^{(0)} \rangle = \sum_m \mid m \rangle \langle m \mid i^{(0)} \rangle = \mid i \rangle \langle i \mid i^{(0)} \rangle + \sum_{m \neq i} \mid m \rangle \langle m \mid i^{(0)} \rangle$.
The wave function renormalization factor is $Z_i = \mid \langle i \mid i^{(0)} \rangle \mid^2$, and hence (with a proper phase convention)
$\mid i^{(0)} \rangle = Z_i^{1/2} \mid i \rangle + \sum_{m \neq i} \mid m \rangle \langle m \mid i^{(0)} \rangle$.
The time-evolution operator in the interaction picture is $U_I(t) = e^{i H_0 t/\hbar}\, U(t)$ (Eq. (5.6.9) in Sakurai with $t_0 = 0$), and hence
$\langle i^{(0)} \mid U_I(t) \mid i^{(0)} \rangle = \langle i^{(0)} \mid e^{i H_0 t/\hbar}\, U(t) \mid i^{(0)} \rangle = e^{i E_i^{(0)} t/\hbar} \langle i^{(0)} \mid U(t) \mid i^{(0)} \rangle$
$= e^{i E_i^{(0)} t/\hbar} (Z_i \langle i \mid U(t) \mid i \rangle + \sum_{m \neq i} \langle m \mid U(t) \mid m \rangle \mid \langle m \mid i^{(0)} \rangle \mid^2)$
$= Z_i\, e^{-i\, (E_i - E_i^{(0)})\, t/\hbar} + \sum_{m \neq i} e^{-i\, (E_m - E_i^{(0)})\, t/\hbar} \left| \langle m \mid i^{(0)} \rangle \right|^2$
If you expand this expression up to $O(V^2)$, you recover precisely the result obtained above. This technique and that below are somehow not discussed in any textbooks I know. If you find one, let me know.

## (b)

Following the same steps as above,
$(\frac{-i}{\hbar})^2 \int_0^t \int_0^{t'} \langle i \,|\, V_I(t')\, V_I(t'') \,|\, i \rangle\, d\,t''\, d\,t' = \frac{-1}{\hbar^2} \int_0^t \int_0^{t'} \sum_m \langle i \,|\, V_I(t') \,|\, m \rangle \langle m \,|\, V_I(t'') \,|\, i \rangle\, d\,t''\, d\,t'$
$= \frac{-1}{\hbar^2} \int_0^t \int_0^{t'} \sum_m V_{i\,m} \cos \omega\, t'\, e^{-i(E_m - E_i)\, t'/\hbar}\, V_{m\,i} \cos \omega\, t''\, e^{-i(E_i - E_m)\, t''/\hbar}\, d\,t''\, d\,t'$
$= \frac{-1}{\hbar^2} \int_0^t \int_0^{t'} (V_{i\,i}{}^2 \cos \omega\, t' \cos \omega\, t'' + \sum_{m \neq i} V_{i\,m} \cos \omega\, t'\, e^{-i(E_m - E_i)\, t'/\hbar}\, V_{m\,i} \cos \omega\, t''\, e^{-i(E_i - E_m)\, t''/\hbar})\, d\,t''\, d\,t'$
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
$\frac{-1}{\hbar^2} \sum_{m \neq i} V_{i\,m}\, V_{m\,i} \int_0^t \int_0^{t'} \cos \omega\, t'\, e^{-i(E_m - E_i)\, t'/\hbar}\, \frac{1}{2} \,(e^{-i(E_i - E_m + \hbar\,\omega)\, t''/\hbar} + e^{-i(E_i - E_m - \hbar\,\omega)\, t''/\hbar})\, d\,t''\, d\,t'$
$= \frac{-1}{\hbar^2} \sum_{m \neq i} V_{i\,m}\, V_{m\,i} \int_0^t \cos \omega\, t'\, e^{-i(E_m - E_i)\, t'/\hbar}\, \frac{1}{2} \left( \frac{e^{-i(E_i - E_m + \hbar\,\omega)\, t'/\hbar} - 1}{-i(E_i - E_m + \hbar\,\omega)/\hbar} + \frac{e^{-i(E_i - E_m - \hbar\,\omega)\, t'/\hbar} - 1}{-i(E_i - E_m - \hbar\,\omega)/\hbar} \right) d\,t'$
$= \frac{-1}{\hbar^2} \sum_{m \neq i} V_{i\,m}\, V_{m\,i} \int_0^t \cos \omega\, t'\, \frac{1}{2} \left( \frac{e^{-i\,\omega t'} - e^{-i(E_m - E_i)\, t'/\hbar}}{-i(E_i - E_m + \hbar\,\omega)/\hbar} + \frac{e^{i\,\omega\, t'} - e^{-i(E_m - E_i)\, t'/\hbar}}{-i(E_i - E_m - \hbar\,\omega)/\hbar} \right) d\,t'$
The terms with $e^{-i(E_m - E_i)\, t'/\hbar}$ oscillate rapidly and can be dropped. Then,
$= \frac{-1}{\hbar^2} \sum_{m \neq i} V_{i\,m}\, V_{m\,i} \int_0^t \frac{1}{4} \,(e^{i\,\omega\, t'} + e^{-i\,\omega\, t'}) \left( \frac{e^{-i\,\omega t'}}{-i(E_i - E_m + \hbar\,\omega)/\hbar} + \frac{e^{i\,\omega\, t'}}{-i(E_i - E_m - \hbar\,\omega)/\hbar} \right) d\,t'$
Only the terms without the oscillatory factors give $O(t)$ contributions,
$= \frac{-i}{\hbar} \sum_{m \neq i} V_{i\,m}\, V_{m\,i}\, \frac{1}{4} \left( \frac{1}{E_i - E_m + \hbar\,\omega} + \frac{1}{E_i - E_m - \hbar\,\omega} \right) t$
$= \frac{-i}{\hbar} \sum_{m \neq i} V_{i\,m}\, V_{m\,i}\, \frac{1}{4}\, \frac{2\,(E_i - E_m)}{(E_i - E_m + \hbar\,\omega)\,(E_i - E_m - \hbar\,\omega)}\, t$
$= \frac{-i}{\hbar}\, \frac{1}{2} \sum_{m \neq i} \frac{|V_{m\,i}|^2\,(E_i - E_m)}{(E_i - E_m)^2 - (\hbar\,\omega)^2}\, t$
Therefore,
$\Delta_i{}^{(2)} = \frac{1}{2} \sum_{m \neq i} \frac{|V_{m\,i}|^2\,(E_i - E_m)}{(E_i - E_m)^2 - (\hbar\,\omega)^2}$ .
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
$\Delta_i{}^{(2)} = \frac{1}{2}\, e^2\, E_0{}^2 \sum_{m \neq i} \frac{|z_{m\,i}|^2\,(E_i - E_m)}{(E_i - E_m)^2 - (\hbar\,\omega)^2}$ .
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 $\int d^3\, x\, \frac{1}{2}\, (E_0 \cos(k\, x - \omega\, t))^2 = \int d^3\, x\, \frac{1}{4}\, E_0{}^2$, where the time average $\langle \cos^2 \omega\, t \rangle = \frac{1}{2}$ is taken. Therefore, it corrects the Lagrangian density as
$\frac{1}{4}\, E_0{}^2 \to \frac{1}{4}\, E_0{}^2 \left(1 - \frac{N}{V}\, 2\, e^2 \sum_{m \neq i} \frac{|z_{m\,i}|^2\,(E_i - E_m)}{(E_i - E_m)^2 - (\hbar\,\omega)^2} \right)$,
where $\frac{N}{V}$ is the number density of the hydrogen atom, and hence the polarizability is
$\alpha = 2\, e^2\, E_0{}^2 \sum_{m \neq i} \frac{|z_{m\,i}|^2\,(E_m - E_i)}{(E_i - E_m)^2 - (\hbar\,\omega)^2}$
which agrees with the static case when $\omega \to 0$.

## *(d)*

With the polarizability and the number density $n$,
$n(\omega) = (1 + \frac{N}{V}\,\alpha)^{1/2} = 1 + \frac{N}{V}\,2\,e^2\,E_0{}^2 \sum_{m \neq i} \frac{|z_{m\,i}|^2 (E_m - E_i)}{(E_i - E_m)^2 - (\hbar\,\omega)^2}$ .
Cleary 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.