## 1. Time-dependent Perturbation Theory.

Find the time dependent dipole moment using:

$$\mu(t) = \langle \Psi(r,t) | ez | \Psi(r,t) \rangle$$

Substitute in the expression for the time-dependent wavefunction:

$$\Psi(r,t) = a_0(t)\varphi_0^{(0)}(r)e^{-iE_0 t/\hbar} + \sum_{n\neq 0}^{\infty} a_n(t)\varphi_n^{(0)}(r)e^{-iE_n t/\hbar}$$

This substitution yields:

$$\mu(t) = \left\langle {}_0(t)\varphi_0^{(0)}(r)e^{-iE_0 t/\hbar} + \sum_{n\neq 0}^{\infty} a_n(t)\varphi_n^{(0)}(r)e^{-iE_n t/\hbar} \middle| ez \middle| {}_0(t)\varphi_0^{(0)}(r)e^{-iE_0 t/\hbar} + \sum_{n\neq 0}^{\infty} a_n(t)\varphi_n^{(0)}(r)e^{-iE_n t/\hbar} \right\rangle$$

We expand the integral into four terms:

$$\mu(t) = \left\langle a_0(t)\varphi_0^{(0)}(r)e^{-iE_0 t/\hbar} \middle| ez \middle| a_0(t)\varphi_0^{(0)}(r)e^{-iE_0 t/\hbar} \right\rangle + \left\langle a_0(t)\varphi_0^{(0)}(r)e^{-iE_0 t/\hbar} \middle| ez \middle| \sum_{n\neq 0}^{\infty} a_n(t)\varphi_n^{(0)}(r)e^{-iE_n t/\hbar} \right\rangle$$
$$+ \left\langle \sum_{n\neq 0}^{\infty} a_n(t)\varphi_n^{(0)}(r)e^{-iE_n t/\hbar} \middle| ez \middle| a_0(t)\varphi_0^{(0)}(r)e^{-iE_0 t/\hbar} \right\rangle + \left\langle \sum_{n\neq 0}^{\infty} a_n(t)\varphi_n^{(0)}(r)e^{-iE_n t/\hbar} \middle| ez \middle| \sum_{n\neq 0}^{\infty} a_n(t)\varphi_n^{(0)}(r)e^{-iE_n t/\hbar} \right\rangle$$

Substitute in the following expression for $a_n$:

$$a_n(t) = \frac{-1}{\hbar}\left\langle \varphi_n^{(0)} \middle| \mathrm{H}^{(1)} \middle| \varphi_0^{(0)} \right\rangle \left[ \frac{e^{i(\omega_{no}+\omega)t} - 1}{\omega_{no}+\omega} + \frac{e^{i(\omega_{no}-\omega)t} - 1}{\omega_{no}-\omega} \right]$$

Note that we use the time independent perturbation $\mathrm{H}^{(1)}$ from:

$$\mathrm{H}^{(1)}(t) = \mathrm{H}^{(1)} 2\cos(\omega t) = e\hat{z}E 2\cos(\omega t)$$

This results in a new expression for the dipole moment:

$$
\begin{aligned}
\mu(t) &= \left|a_0(t)\right|^2 \left\langle \varphi_0^{(0)}(r) \middle| ez \middle| \varphi_0^{(0)}(r) \right\rangle \\
&+ \frac{-a_0(t)^*}{\hbar} \sum_{n\neq 0}^{\infty} e^{i(E_0-E_n)t/\hbar} \left\langle \varphi_n^{(0)}(r) \middle| E_z ez \middle| \varphi_0^{(0)}(r) \right\rangle \left\langle \varphi_0^{(0)}(r) \middle| ez \middle| \varphi_n^{(0)}(r) \right\rangle \left[ \frac{e^{i(\omega_{no}+\omega)t}-1}{\omega_{no}+\omega} + \frac{e^{i(\omega_{no}-\omega)t}-1}{\omega_{no}-\omega} \right] \\
&+ \frac{-a_0(t)}{\hbar} \sum_{n\neq 0}^{\infty} e^{-i(E_0-E_n)t/\hbar} \left\langle \varphi_n^{(0)}(r) \middle| E_z ez \middle| \varphi_0^{(0)}(r) \right\rangle \left\langle \varphi_n^{(0)}(r) \middle| ez \middle| \varphi_0^{(0)}(r) \right\rangle \left[ \frac{e^{-i(\omega_{no}+\omega)t}-1}{\omega_{no}+\omega} + \frac{e^{-i(\omega_{no}-\omega)t}-1}{\omega_{no}-\omega} \right] \\
&+ \left\langle \sum_{n\neq 0}^{\infty} \left[ \frac{e^{-i(\omega_{no}+\omega)t}-1}{\omega_{no}+\omega} + \frac{e^{-i(\omega_{no}-\omega)t}-1}{\omega_{no}-\omega} \right] \left\langle \varphi_n^{(0)}(r) \middle| E_z ez \middle| \varphi_0^{(0)}(r) \right\rangle \varphi_n^{(0)}(r) \frac{e^{-iE_n t/\hbar}}{\hbar} \right| \\
&\quad ez \left| \sum_{n\neq 0}^{\infty} \left[ \frac{e^{-i(\omega_{no}+\omega)t}-1}{\omega_{no}+\omega} + \frac{e^{-i(\omega_{no}-\omega)t}-1}{\omega_{no}-\omega} \right] \left\langle \varphi_n^{(0)}(r) \middle| E_z ez \middle| \varphi_0^{(0)}(r) \right\rangle \varphi_n^{(0)}(r) \frac{e^{-iE_n t/\hbar}}{\hbar} \right\rangle
\end{aligned}
$$

By ignoring terms that are not linear in $E_z$ (because only terms linear in $E_0 = E_z$ can be linear in $E(t) = 2E_0 \cos\omega t$) and noting that $\omega_{n0}\hbar = E_n - E_0$ we obtain:

$$
\begin{aligned}
\mu(t) &= \frac{-1}{\hbar} \sum_{n\neq 0}^{\infty} e^{i\omega_{n0}t} \left\langle \varphi_n^{(0)}(r) \middle| E_z ez \middle| \varphi_0^{(0)}(r) \right\rangle \left\langle \varphi_0^{(0)}(r) \middle| ez \middle| \varphi_n^{(0)}(r) \right\rangle \left[ \frac{e^{i(\omega_{no}+\omega)t}-1}{\omega_{no}+\omega} + \frac{e^{i(\omega_{no}-\omega)t}-1}{\omega_{no}-\omega} \right] \\
&+ \frac{-1}{\hbar} \sum_{n\neq 0}^{\infty} e^{-i\omega_{n0}t} \left\langle \varphi_n^{(0)}(r) \middle| E_z ez \middle| \varphi_0^{(0)}(r) \right\rangle \left\langle \varphi_n^{(0)}(r) \middle| ez \middle| \varphi_0^{(0)}(r) \right\rangle \left[ \frac{e^{-i(\omega_{no}+\omega)t}-1}{\omega_{no}+\omega} + \frac{e^{-i(\omega_{no}-\omega)t}-1}{\omega_{no}-\omega} \right] \\
&= 2\,\mathrm{Re}\left[ \frac{-1}{\hbar} \sum_{n\neq 0}^{\infty} e^{i\omega_{n0}t} \left\langle \varphi_n^{(0)}(r) \middle| E_z ez \middle| \varphi_0^{(0)}(r) \right\rangle \left\langle \varphi_0^{(0)}(r) \middle| ez \middle| \varphi_n^{(0)}(r) \right\rangle \left[ \frac{e^{i(\omega_{no}+\omega)t}-1}{\omega_{no}+\omega} + \frac{e^{i(\omega_{no}-\omega)t}-1}{\omega_{no}-\omega} \right] \right] \\
&= \frac{-2E_z}{\hbar} \mathrm{Re}\left[ \sum_{n\neq 0}^{\infty} \left| \left\langle \varphi_0^{(0)}(r) \middle| ez \middle| \varphi_n^{(0)}(r) \right\rangle \right|^2 \left[ \frac{\omega_{no}\left[\left(e^{i\omega t}+e^{-i\omega t}\right)-\left(2e^{-i\omega_{no}t}\right)\right]-\omega\left(e^{i\omega t}-e^{-i\omega t}\right)}{\omega_{no}^2-\omega^2} \right] \right] \\
&= \frac{-2E_z}{\hbar} \mathrm{Re}\left[ \sum_{n\neq 0}^{\infty} \frac{\left| \left\langle \varphi_0^{(0)}(r) \middle| ez \middle| \varphi_n^{(0)}(r) \right\rangle \right|^2}{\omega_{no}^2-\omega^2} \left[ 2\omega_{no}\cos\omega t - 2\omega_{no}\left(\cos\omega_{no}t + i\sin\omega_{no}t\right) - i2\omega\sin\omega t \right] \right] \\
&= \frac{-2E_z}{\hbar} \sum_{n\neq 0}^{\infty} \frac{\left| \left\langle \varphi_0^{(0)}(r) \middle| ez \middle| \varphi_n^{(0)}(r) \right\rangle \right|^2}{\omega_{no}^2-\omega^2} \left[ 2\omega_{no}\cos\omega t - 2\omega_{no}\cos\omega_{no}t \right]
\end{aligned}
$$

Since we're only interested in the term which is linear in $E(t) = 2E_0\cos\omega t$, we ignore the second term and get:

$$
\begin{aligned}
\mu(t) &= \frac{-2E_z}{\hbar} \sum_{n\neq 0}^{\infty} \frac{\left| \left\langle \varphi_0^{(0)}(r) \middle| ez \middle| \varphi_n^{(0)}(r) \right\rangle \right|^2}{\omega_{no}^2-\omega^2} 2\omega_{no}\cos\omega t \\
&= \frac{-2E(t)}{\hbar} \sum_{n\neq 0}^{\infty} \frac{\omega_{no} \left| \left\langle \varphi_0^{(0)}(r) \middle| ez \middle| \varphi_n^{(0)}(r) \right\rangle \right|^2}{\omega_{no}^2-\omega^2}
\end{aligned}
$$

Finally, we find $\alpha(\omega)$ using:

$$\alpha(\omega)=\frac{\mu}{E(t)}$$

Substituting our expression for the dipole moment in terms of $E(t)$ gives our final result:

$$\alpha(\omega)=\frac{-2}{\hbar}\sum_{n\neq 0}^{\infty}\frac{-2\omega_{no}}{\hbar}\frac{\left|\left\langle\varphi_0^{(0)}(r)\middle|ez\middle|\varphi_n^{(0)}(r)\right\rangle\right|^2}{\omega_{no}^2-\omega^2}$$

2. **Hydrogen in a Magnetic Field.**

**a.** The motion of an electron about the nucleus constitutes an electric current, which produces a dipole moment that can interact with an external magnetic field. For the motion of the electron, we know $vt = 2r\pi$, where $v$ is the speed of the electron, $t$ is the time it takes to make one revolution, and $r$ is the radius of the orbit.

For a dipole moment, $\mu = IA$. Since $I = \frac{q}{t}$, we can write

$$\mu = \frac{qv}{2\pi r}\pi r^2 = \frac{qvr}{2}.$$

Writing $\mu$ as a vector,

$$\vec{\mu} = \frac{q(\vec{r}\times\vec{v})}{2} = \frac{q(\vec{r}\times\vec{p})}{2m} = \frac{q\vec{L}}{2m}.$$

We know:

$$|L| = \hbar[l(l+1)]^{\frac{1}{2}},$$

So:

$$|\mu| = \frac{|e|\hbar}{2m}[l(l+1)]^{\frac{1}{2}} = \beta_e[l(l+1)]^{\frac{1}{2}},$$

where $\beta_e$ is the Bohr magneton:

$$\beta_e = \frac{|e|\hbar}{2m_e}.$$

Its units are $\frac{J}{T}$.

**b.** The potential energy of a dipole in a magnetic field is $U = -\mu \cdot B$. Since our magnetic field is pointing in the $z$ direction, only the $z$ component of $\mu$ will interact with it. The new Hamiltonian will just be the one for hydrogen with no magnetic field plus the new potential due to this interaction:

$$\hat{H} = \hat{H}_0 + U = \hat{H}_0 - B_z\mu_z = \hat{H}_0 + \frac{|e|\hbar}{2m}\hat{L}_z B_z = \hat{H}_0 + \frac{\beta_e B_z}{\hbar}\hat{L}_z$$

Because the hydrogenlike wavefunctions are eigenfunctions of $\hat{H}_0$ and $\hat{L}_z$, they will still be eigenfunctions for this Hamiltonian. Applying the Hamiltonian to the wavefunctions gives:

$$\hat{H}\psi_{nlm} = \hat{H}_0\psi_{nlm} + \frac{\beta_e B_z}{\hbar}\hat{L}_z\psi_{nlm},$$

So

$$E\psi_{nlm} = E_n^0\psi_{nlm} + \beta_e B_z m\psi_{nlm}$$

And:

$$E = E_n^0 + \beta_e B_z m.$$

**c.** Because $m = 0$ for *s* orbitals, the energies of the 1*s* and 2*s* will be unchanged by the magnetic field. The 2*p*, however, will become degenerate. The energy of the $m = 1$ orbital will be raised by $\beta_e B_z$, while the $m = -1$ will be lowered by the same factor.

For a magnetic field of magnitude 15T, the splitting will be 1.391 x $10^{-22}$J. The difference in energy between unperturbed 1*s* and 2*p* hydrogen orbitals is 1.635 x $10^{-18}$J, so the splitting is about .01% of the energy difference.

**d.** The $l = 2$ state of hydrogen has 5 possible values for *m*, while the $l = 3$ state has 7. So the total number of possible transitions is 35.

If $\Delta m = 0$, each orbital has only one choice of where it can go, so the possible number of transitions is 5. If $\Delta m = \pm 1$, each orbital has two possible destinations, so there are 10 possible transitions.

The quantum number *m* indicates the projection of angular momentum along the *z* axis, and therefore the component of motion of the electron in the *xy* plane. If the electric field vector of the light is parallel to the external magnetic field, and, therefore, $L_z$, it is perpendicular to the component of motion in the *xy* plane and will not be able to exert any torque to change it. So the value of the *z* projection of angular momentum, and hence *m*, will not be changed.

If the electric field vector of the light is perpendicular to the *z* axis, it can effect the motion of the electron in the *xy* plane and therefore change $L_z$ and *m*.