SQ18 Substitute (4) and (5) into (2) and (3)

$$i\hbar \frac{d}{dt} a_1 = (a_1^{(0)} + \lambda a_1^{(1)} + \dots)\langle \psi_1|\lambda H'|\psi_1\rangle + (a_2^{(0)} + \lambda a_2^{(1)}+\dots)\langle\psi_1|\lambda H'|\psi_2\rangle e^{i\frac{E_1-E_2}{\hbar}t}$$

$$= \underbrace{a_1^{(0)}\langle 1|\lambda H'|1\rangle + a_2^{(0)}\langle 1|\lambda H'|2\rangle e^{i\frac{E_1-E_2}{\hbar}t}}_{\propto\lambda^1} + \lambda\underbrace{\left(a_1^{(1)}\langle 1|\lambda H'|1\rangle + a_2^{(1)}\langle 1|\lambda H'|2\rangle e^{i\frac{E_1-E_2}{\hbar}t}\right)}_{\propto \lambda^2}$$

Similarly,

$$i\hbar \frac{d}{dt}a_2 = a_2^{(0)}\langle 2|\lambda H'|2\rangle + a_1^{(0)}\langle 2|\lambda H'|1\rangle e^{i\frac{E_2-E_1}{\hbar}t} + \lambda\left(a_2^{(1)}\langle 2|\lambda H'|2\rangle + a_1^{(1)}\langle 2|\lambda H'|1\rangle e^{i\frac{E_2-E_1}{\hbar}t}\right)$$

Now rewrite $\frac{d}{dt}a_1 = \frac{d}{dt}a_1^{(0)} + \lambda\frac{d}{dt}a_1^{(1)} + \dots\dots$

$\frac{d}{dt}a_2 = \frac{d}{dt}a_2^{(0)} + \lambda\frac{d}{dt}a_2^{(1)} + \dots\dots$

And compare terms with same order in λ.

$\left.\begin{array}{l} i\hbar\frac{d}{dt}a_1^{(0)} = 0\lambda^0 \\ i\hbar\frac{d}{dt}a_2^{(0)} = 0\lambda^0 \end{array}\right\}$ There are no λ^0 terms on R.H.S. as the lowest order is contributed by $\langle i|\lambda H'|j\rangle = V_{ij}$

$\Rightarrow a_1^{(0)} = a_1(0)$ Given by initial conditions

$a_2^{(0)} = a_2(0)$

$\lambda i\hbar \frac{d}{dt}a_1^{(1)} = a_1^{(0)}V_{11} + a_2^{(0)}V_{12}e^{i\frac{E_1-E_2}{\hbar}t}$ where $a_1^{(0)}$ and $a_2^{(0)}$ appear on the R.H.S

$\lambda i\hbar \frac{d}{dt}a_2^{(1)} = a_2^{(0)}V_{22} + a_1^{(0)}V_{21}e^{i\frac{E_2-E_1}{\hbar}t}$ of $\frac{d}{dt}a_1^{(1)}$ and $\frac{d}{dt}a_2^{(1)}$

Now we use $a_1(0)=1$, $a_2(0)=0$, (i.e. initially the state is $|1\rangle$)

$$\frac{d}{dt}a_2^{(1)}(t) = -\frac{iV_{21}}{\hbar}e^{i\frac{E_2-E_1}{\hbar}t}$$

$$a_2^{(1)}(t) = \frac{1}{i\hbar}\int_0^t \left(\int \psi_2^* H'\psi_1 \, d^3r\right) e^{i\frac{E_2-E_1}{\hbar}t'}dt'$$

In 1-D, $a_2^{(1)}(t) = \frac{1}{i\hbar}\int_0^t \int_{-\infty}^{\infty} \psi_2^* e^{i\frac{E_2}{\hbar}t'} H' e^{-i\frac{E_1}{\hbar}t'}\psi_1 \, dx)\, dt'$

which is just (13) in class notes.

SQ19 a) $a_2(t) \propto \int \psi^*_{200}(\vec{r})\, \vec{r}\, \psi_{100}(\vec{r})\, d^3r$

rewrite $\vec{r}$ with $\hat{x}, \hat{y}, \hat{z}$ which are constant for integration.

$$\vec{r} = r\sin\theta\cos\phi\,\hat{x} + r\sin\theta\sin\phi\,\hat{y} + r\cos\theta\,\hat{z}$$

Consider only the θ and ϕ part of integral.

$$a_2(t) \propto \int_0^{2\pi}\int_0^{\pi} (\sin\theta\cos\phi\,\hat{x} + \sin\theta\sin\phi\,\hat{y} + \cos\theta\,\hat{z})\sin\theta\, d\theta\, d\phi.$$

$$= \underbrace{\int_0^{2\pi}\cos\phi\, d\phi}_{=0} \underbrace{\int_0^{\pi}\sin^2\theta\, d\theta}_{=0}\,\hat{x} + \underbrace{\int_0^{2\pi}\sin\phi\, d\phi}_{=0} \int_0^{\pi}\sin^2\theta\, d\theta\,\hat{y} + \int_0^{2\pi}\underbrace{\int_0^{\pi}\cos\theta\, d\theta}_{=0}\, d\phi\,\hat{z}$$

$= 0$

$\therefore$ Without evaluating the integral over r, we could determine that $\alpha_2(t) = 0$, meaning the transition is forbidden.

b) i $\int \psi^*_{211}(\vec{r})\, \vec{r}\, \psi_{100}(\vec{r})\, d^3r$

$$= \int \underbrace{\frac{1}{\sqrt{2\pi}} e^{-i\phi} \frac{\sqrt{3}}{2}\sin\theta \frac{1}{2\sqrt{6a_0^3}} \frac{r}{a_0} e^{-\frac{r}{2a_0}}}_{\psi^*_{211}} \cdot \underbrace{(r\sin\theta\cos\phi\,\hat{x} + r\sin\theta\sin\phi\,\hat{y} + r\cos\theta\,\hat{z})}_{\vec{r}} \underbrace{\frac{1}{\sqrt{2\pi}}\frac{1}{\sqrt{2}}\frac{2}{a_0^{\frac{3}{2}}} e^{-\frac{r}{a_0}}}_{\psi_{100}} d^3r$$

$$= \frac{1}{2\pi}\frac{1}{4a_0^4} \int_0^{\infty} r^4 e^{-\frac{3r}{2a_0}} dr \cdot \int_0^{2\pi}\int_0^{\pi} \sin^2\theta(\sin\theta(\cos\phi\,\hat{x} + \sin\phi\,\hat{y}) + \cos\theta\,\hat{z}) e^{-i\phi}\, d\theta\, d\phi$$

$$= \frac{1}{8\pi a_0^4} \frac{24}{\left(\frac{3}{2a_0}\right)^5} \cdot \int_0^{2\pi} \frac{4}{3}(\cos\phi\,\hat{x} + \sin\phi\,\hat{y})(\cos\phi - i\sin\phi)\, d\phi$$

$$= \frac{32}{81\pi} a_0 \quad \frac{4}{3}(\pi\hat{x} - i\pi\hat{y})$$

$$= \frac{128}{243} a_0 (\hat{x} - i\hat{y}) \quad \text{a complex vector.}$$

ii Instead of $\vec{r}$, we have $\vec{z}$ instead

$$\hat{H}' \propto \int \psi^*_{2p}(\vec{r})\, \vec{z}\, \psi_{1s}(\vec{r})\, d^3r$$

From i) we see that $\vec{z}$ actually does not contribute to transition from 1s to 2p state of $m_\ell = 1$.

For z component to be non-zero.

Given the initial state 1s, final state 2p and stimulation $e\mathcal{E}\vec{z}$, only condition such that $z_{2p,1s} \neq 0$ would be change m_ℓ.

$\psi(2,1,m_\ell) \propto e^{m_\ell\phi}$, $z_{2p,1s} \propto \int_0^{2\pi} e^{m_\ell\phi}\, d\phi \neq 0$ if $m_\ell = 0$, i.e. from $|1,0,0\rangle$ to $|2,1,0\rangle$

From $a_2(t) \propto \int \psi^*_{2p}(r)\, \vec{z}\, \psi_{1s}(r)\, d^3r = 0$, we could argue that the transition probability $= 0$ and $a_2^*(t) = \int \psi_{1s}(r)\, \vec{z}\, \psi^*_{2p}(r)\, d^3r = 0$ follows naturally, meaning both $|1,0,0\rangle$ to $|2,1,1\rangle$ and $|2,1,1\rangle$ to $|1,0,0\rangle$ are forbidden by only using linearly polarized light.

b) iii For $\vec{e}^{+} \propto (\hat{x}+i\hat{y})$

$$a_2(t) \propto \int \psi_{211}^{*} \; \vec{r}\cdot(\hat{x}+i\hat{y})\,\psi_{100}\, e^{-i\omega t} d^3r$$

$$= e^{-i\omega t}\left(\int \psi_{211}^{*}\, \vec{r}\, \psi_{100}\, d^3r\right)\cdot(\hat{x}+i\hat{y})$$

$$= e^{-i\omega t}\, \frac{128}{243} a_0 (\hat{x}-i\hat{y})(\hat{x}+i\hat{y})$$ Using result from ii)

$$= \frac{256}{243} a_0\, e^{-i\omega t}$$

$$|\alpha_2(\tau)|^2 = \left(\frac{256}{243} a_0\right)^2 > 0.$$

Therefore, there are non-zero probability for this circularly polarised light to stimulate transition from $|1,0,0\rangle$ to $|2,1,1\rangle$