1. (a)

Valence electrons are confined in region of size a

$\rightarrow$ uncertainty in spatial coordinates

$$\Delta x \simeq a$$

uncertainty principle $\Delta p \, \Delta x \approx \hbar$

$$\rightarrow \quad \Delta p \approx \frac{\hbar}{a}$$

the valence electrons are orbiting around so the mean momentum should be 0 $\Rightarrow \langle p \rangle = 0$

$$\Delta p = \sqrt{\langle p^2 \rangle - \underbrace{\langle p \rangle^2}_{=0}} = \sqrt{\langle p^2 \rangle} \approx p$$

$$\Rightarrow \quad p^2 \approx (\Delta p)^2 \approx \frac{\hbar^2}{a^2}$$

Electronic energy should be on the order of kinetic energy of ~~elect~~ electrons

$\therefore$ The energy of electrons will be of the order

$$E_e \approx \frac{p^2}{2m} \approx \boxed{\frac{\hbar^2}{2ma}}$$

(b) potential energy between two nuclei are assumed to have the form (classical oscillator)

$$U(x) = \cancel{\frac{1}{2}\mu\omega_v^2 x^2} \; \frac{1}{2}\mu\omega_v^2 x^2 \qquad \left(\mu = \frac{M_1 M_2}{M_1 + M_2}\right)$$

As $x \simeq a$, $U(x)$ should be on the order of electronic energy because the spatial extent of

the two interactions are comparable.
So $U(a) \simeq E_e$

$\frac{1}{2}\mu\omega_v^2 a^2 \simeq$ binding energy

$\Rightarrow \frac{1}{2}\mu\omega_v^2 a^2 \simeq \frac{\hbar^2}{2ma^2}$ $\simeq E_e$ = electron energy

most binding comes from electrons

$\rightarrow \omega_v \simeq \sqrt{\frac{\hbar^2}{m\mu a^4}} \simeq \frac{1}{\hbar}\sqrt{\frac{m}{\mu}}\frac{\hbar^2}{ma^2} = \frac{1}{\hbar}\sqrt{\frac{m}{\mu}} E_e$

Vibrational energy

$$E_v \simeq \hbar\omega_v \simeq \sqrt{\frac{m}{\mu}} E_e$$ ✓

(c) The rotational energy is on the order of

$$E_r \simeq \frac{1}{2} I \omega_r^2$$

where I = moment of inertia $\simeq \mu a^2$

Angular momentum on the order of $\hbar$

$I\omega_r \simeq \mu a^2 \omega_r \simeq \hbar \rightarrow \omega_r \simeq \frac{\hbar}{\mu a^2}$

$\rightarrow E_r \simeq \frac{1}{2}(\mu a^2)\left(\frac{\hbar}{\mu a^2}\right)^2 \simeq \frac{\hbar^2}{2\mu a^2}$

$\simeq \frac{m}{\mu}\left(\frac{\hbar^2}{2ma^2}\right) = \frac{m}{\mu} E_e$ ✓

(d) For ~~HCl~~ HCl ~~atom~~ molecule

$a \sim R_0 = 0.128\,nm = 0.128\times10^{-9}\,m$

$m = m_e = 9.11\times10^{-31}\,kg$

$M_1 = M(H) = (1)m_p + (0)m_n = 1.67\times10^{-27}\,kg$

$M_2 = M(Cl) = 17m_p + 18m_n = 5.85\times10^{-26}\,kg$

$$\mu = \frac{M_1 M_2}{M_1+M_2} = 1.62\times10^{-27}\,kg$$

energy $E_e \simeq \frac{\hbar}{2ma}$, $E_v \simeq \sqrt{\frac{m}{\mu}}E_e$, $E_r \simeq \frac{m}{\mu}E_e$

frequency $\omega_e \simeq \frac{E_e}{\hbar}$, $\omega_v = \frac{E_v}{\hbar}$, $\omega_r \simeq \frac{E_r}{\hbar}$

$f_e = \frac{E_e}{h}$ $f_v = E_v/h$ $f_r = E_r/h$

time scale ~~$\tau_e \simeq \frac{1}{\omega_e}$, $\tau_v = \frac{1}{\omega_v}$, $\tau_r = \frac{1}{\omega_r}$~~

$\tau_e = \frac{1}{f_e}$ $\tau_v = \frac{1}{f_v}$ $\tau_r = \frac{1}{f_r}$

	electric	vibrational	rotational
energy	$3.69\times10^{-19}\,J$ $\simeq 2.3\,eV$	$8.86\times10^{-21}\,J$ $\simeq 0.055\,eV$	$2.13\times10^{-22}\,J$ $\simeq 0.0013\,eV$
frequency	~~$3.51\times10^{15}\,Hz$~~ $5.87\times10^{14}\,Hz$	~~$8.44\times10^{13}\,Hz$~~ $1.34\times10^{13}\,Hz$	~~$2.03\times10^{12}\,Hz$~~ $3.23\times10^{11}\,Hz$
time scale	~~$2.85\times10^{-16}\,s$~~ $1.79\times10^{-15}\,s$	~~$1.19\times10^{-14}\,s$~~ $7.47\times10^{-14}\,s$	~~$4.93\times10^{-13}\,s$~~ $3.09\times10^{-12}\,s$

(e)

$$\bar{E} = E_e + (\nu + \tfrac{1}{2})\hbar\omega_\nu + B_r K(K+1)$$

→ estimate:

$$\omega_\nu \simeq \left(\frac{\hbar^2}{\mu m R_0^4}\right)^{\frac{1}{2}} = \underline{1.67 \times 10^{14}\ Hz}$$

measured value:

$$\omega_\nu = (2090 \times 100)\ 2\pi c$$

$$= (2090 \times 100) \cdot 2\pi \cdot 3 \times 10^8 = \underline{3.94 \times 10^{14}\ Hz}$$

They agree to the same order of magnitude.

→ estimate

~~B_r~~

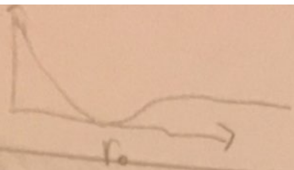
$$B_r \simeq \frac{\hbar^2}{2\mu R_0^2} = \underline{2.08 \times 10^{-22}\ J}$$

measured value

$$B_r = (20.8 \times 100) \cdot c \cdot h$$

$$= \underline{4.14 \times 10^{-22}\ J}$$

They agree to the same order of magnitude



2. (a) Mores potential $V(r) = D[1-e^{-\beta(r-r_0)}]^2$

equilibrium :

$$0 = \frac{dV}{dr} = 2D[1-e^{-\beta(r-r_0)}](\beta e^{-\beta(r-r_0)})$$

$$\Rightarrow \quad r = r_0$$

Small perturbation away from $r=r_0$, $\delta r = r - r_0$

$$\Rightarrow V(r) = \underbrace{V(r_0)}_{0} + \underbrace{\left.\frac{dV}{dr}\right|_{r=r_0}}_{=0 \because \text{ equilibrium}} (r-r_0) + \frac{1}{2!}\left.\frac{d^2V}{dr^2}\right|_{r=r_0} (r-r_0)^2 + O(\delta r^3)$$

$$= \frac{1}{2}\left.\frac{d^2V}{dr^2}\right|_{r=r_0} (r-r_0)^2$$

$$= \frac{1}{2}\frac{d}{dr}\left(2\beta D(1-e^{-\beta(r-r_0)})(e^{-\beta(r-r_0)})\right)\Big|_{r=r_0} (r-r_0)^2$$

$$= \beta D \frac{d}{dr}\left(e^{-\beta(r-r_0)} - e^{-2\beta(r-r_0)}\right)\Big|_{r=r_0} (r-r_0)^2$$

$$= \beta D\left(-\beta e^{-\beta(r-r_0)} + 2\beta e^{-2\beta(r-r_0)}\right)\Big|_{r=r_0} (r-r_0)^2$$

$$= \beta D(2\beta-\beta)(r-r_0)^2 = \underline{\beta^2 D (r-r_0)^2}$$

Classical Harmonic Osuillator

$$V(r) = \frac{1}{2}\mu\omega_v^2 \cancel{(r-r_0)^2} = \beta^2 D \cancel{(r-r_0)^2}$$

$$\Rightarrow \boxed{\omega_v = \sqrt{\frac{2\beta^2 D}{\mu}}}$$

(b)

$$V_{eff}(r) = D[1-e^{-\beta(r-r_0)}]^2 + \frac{\hbar^2 k(k+1)}{2\mu r^2}$$

New equilibrium:

$$0 = \frac{dV_{eff}(r)}{dr} = 2\beta D(1-e^{-\beta(r-r_0)})e^{-\beta(r-r_0)} - \frac{\hbar^2 k(k+1)}{\mu r^3}$$

~~Assume ... then~~

For small perturbation $\beta(r-r_0) \ll 1$, then

$$e^{-\beta(r-r_0)} \simeq 1-\beta(r-r_0)$$

let $\delta r = r - r_0$

$\Rightarrow r = r_0 + \delta r$

$$\frac{1}{r^3} = r^{-3} = (r_0+\delta r)^{-3} = r_0^{-3}(1+\frac{\delta r}{r_0})^{-3}$$

$$= \frac{1}{r_0^3}(1+\delta r/r_0)^{-3} \simeq \frac{1}{r_0^3}(1-\frac{3\delta r}{r_0})$$

$$\rightarrow 0 = 2\beta D(1-\underbrace{(1-\beta\delta r)}_{\beta\delta r})(1-\beta\delta r) - \frac{\hbar^2 k(k+1)}{\mu r_0^3}(1-\frac{3\delta r}{r_0})$$

$$= 2\beta^2 D\delta r - 2\beta^3 D\delta r^2 - \frac{\hbar^2 k(k+1)}{\mu r_0^3} + \frac{3\hbar^2 k(k+1)}{\mu r_0^4}\delta r$$

neglect term that involves δr^2

$$\rightarrow (2\beta^2 D + \frac{3\hbar^2 k(k+1)}{\mu r_0^4})\delta r = \frac{\hbar^2 k(k+1)}{\mu r_0^3}$$

$$\rightarrow \quad \delta r = \frac{\dfrac{\hbar^2 k(k+1)}{2\beta^2 D r_0^3 \mu}}{1 + \dfrac{3\hbar^2 k(k+1)}{\mu 2\beta^2 D r_0^3}} = r - r_0$$

$\rightarrow$ ~~$r \approx$~~ r_0

$$r = r_0 + \underbrace{\frac{\hbar^2 k(k+1)}{2\beta^2 D r_0^3 \mu}}_{O\left(\frac{V_r}{V_v}\right)} \Big(1 - \underbrace{\frac{3\hbar^2 k(k+1)}{2\beta^2 D r_0^3 \mu}}_{O\left(\frac{V_r}{V_v}\right)^2}\Big)$$

(V_r ~ rotational energy , V_v ~ vibration potential ~~energy~~)

$\because$ rotational energy $V \ll$ vibrational potential ~~energy~~,

$\rightarrow$ neglect $O\left(\frac{V_r}{V_v}\right)^2$ term

$$\rightarrow \quad \boxed{r_k = r_0 + \frac{\hbar^2 k(k+1)}{2\beta^2 D r_0^3 \mu}}$$ is new equilibrium position.

(c)

Now the ~~next potential~~ energy in equilibrium is

$$E = V(r_k) + \frac{\hbar^2 k(k+1)}{2\mu r_k^2}$$

$$= V(r_0) + \underbrace{\frac{dV}{dr}\Big|_{r_0}}_{0}(r_k - r_0) + \frac{\hbar^2 k(k+1)}{2\mu r_0^2}\left(1 - \frac{2(r_k - r_0)}{r_0}\right)$$

$$= \underbrace{V(r_0) + \frac{\hbar^2 k(k+1)}{r_0^2}}_{E_0} - \underbrace{\frac{\hbar^2 k(k+1)}{\mu r_0^3}(r_k - r_0)}_{\Delta E}$$

$\rightarrow E = E_0 + \Delta E$, where

$$E_0 = V(r_0) + \frac{\hbar^2 K(K+1)}{2\mu r_0^2}$$ is energy

of original separation.

$\rightarrow$ The new term is thus

$$\Delta E = -\frac{\hbar^2 K(K+1)}{\mu r_0^3}(r_K - r_0)$$

$$= -\frac{\hbar^2 K(K+1)}{\mu r_0^3}\left(\frac{\hbar^2 K(K+1)}{2\beta^2 D r_0^3 \mu}\right)$$

$$= -\frac{\hbar^4}{2\beta^2 D \mu^2 r_0^6} K^2(K+1)^2$$

$$\omega_v^2 = \frac{2\beta^2 D}{\mu}$$

$$2\beta^2 D \mu^2 = \omega_v^2 \mu^3$$

$$= -\frac{\hbar^4}{\omega_v^2 \mu^3 r_0^6} K^2(K+1)^2$$

second order neglect.

$$V = D\beta^2 x^2 + \frac{\hbar^2 K(K+1)}{2\mu r_0^2}\left(1 - \frac{2x}{r_0}\right)$$

$$= \frac{-8}{\hbar^2 \omega_v^2}\left(\frac{\hbar^6}{8\mu^3 r_0^6}\right) K^2(K+1)^2$$

0th order : $\frac{\hbar^2 K(K+1)}{2\mu r_0^2}$

$$= -\frac{8}{\hbar^2 \omega_v^2}\underbrace{\left(\frac{\hbar^2}{2\mu r_0^2}\right)}_{B_1}{}^3 K^2(K+1)^2$$

1st order : $\frac{\hbar^2 K^2 (K+1)^2}{\mu^2 D \beta^2 r_0^6}$

$$= -B_1 K^2 (K+1)^2$$

3.

(a)

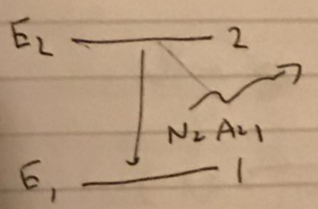
The principle of detailed balance : in thermal equilibrium the transitions between any pair of levels are in dynamic equilibrium.

For arbitrary atomic levels 1 and 2,

→ rate of absorption = the rate of spontaneous emission + the rate of stimulated emission (per volume)

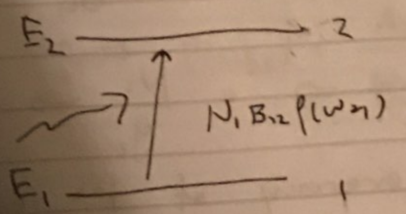
→ rate of spontaneous emission per volume

$$= \underbrace{N_2}_{\text{number density in level 2}} \underbrace{A_{21}}_{\text{Einstein A coefficient}}$$



→ rate of absorption per volume

$$= \underbrace{N_1}_{\text{number density of level 1}} \underbrace{B_{12}}_{\text{einstein B coefficient}} \underbrace{\rho(\omega_{21})}_{\text{energy density of radiation at frequency } \omega_{21} = (E_2 - E_1)/\hbar}$$



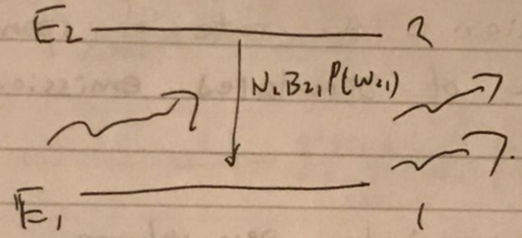
→ rate of stimulated emission per volume

$$= N_2 B_{21} \rho(\omega_{21})$$

number density of level 2

einstein B coefficient

energy density of radiation at frequency $\omega_{21} = (E_2 - E_1)/\hbar$



$$\therefore \quad N_2 A_{21} + N_2 B_{21} \rho(\omega_{21}) = N_1 B_{12} \rho(\omega_{21})$$

$$\rightarrow \quad \frac{N_2}{N_1} = \frac{B_{12} \rho(\omega_{21})}{B_{21} \rho(\omega_{21}) + A_{21}}$$

(b) At very large energy density A_{21} is negligible compare to $B_{21} \rho(\omega_{21})$

$$\therefore \quad \frac{N_2}{N_1} \rightarrow \frac{B_{12}}{B_{21}}$$

As will be proven in (c), $\frac{B_{12}}{B_{21}} = \frac{g_2}{g_1}$

$$\rightarrow \quad \frac{N_2}{N_1} \rightarrow \frac{g_2}{g_1} \quad \Rightarrow \quad \frac{N_2}{g_2} \rightarrow \frac{N_1}{g_1}$$

(g_i is the degeneracy of ith level)

$\therefore \frac{N_2}{g_2}$ approaches $\frac{N_1}{g_1}$ but still cannot go larger than it.

population inversion is ~~the~~ that the population per state of the ~~lower~~ upper level > the lower level

$\therefore$ need $\frac{N_2}{g_2} > \frac{N_1}{g_1}$ ✓

→ Thus population inversion cannot be achieved in thermal equilibrium even in very high energy density. ✓

(c) In thermal radiation:

$$N_i = \cancel{g_i} \frac{g_i}{Z} \exp(-E_i/k_B T)\, N$$

(N = total number density of system
Z = partition function)

$$\therefore \frac{N_2}{N_1} = \frac{g_2 \exp(-\frac{E_2}{k_B T})}{g_1 \exp(-\frac{E_1}{k_B T})} = \frac{g_2}{g_1} \exp(-\frac{\hbar \omega_{21}}{k_B T})$$

$$\underbrace{}_{\hbar\omega_{21} = E_2 - E_1}$$

$$\because N_2 B_{21} \rho(\omega_{21}) + N_2 A_{21} = N_1 B_{12} \rho(\omega_{21})$$

$$\therefore \cancel{\rho(\omega)} \; \rho(\omega_{21}) = \frac{A_{21}/B_{21}}{\frac{N_1}{N_2}\frac{B_{12}}{B_{21}} - 1}$$ ✓

Hence $\rho(\omega_{21}) = \dfrac{A_{21}/B_{21}}{\frac{g_1}{g_2}\frac{B_{12}}{B_{21}}\exp\left(\frac{\hbar\omega_{21}}{k_BT}\right) - 1}$

Compare with the Black Body radiation

$$\rho(\omega) = \frac{\hbar\omega^3}{\pi^2c^3}\left(\frac{1}{\exp\left(\frac{\hbar\omega}{k_BT}\right)-1}\right)$$

we get :

$$\frac{A_{21}}{B_{21}} = \frac{\hbar\omega_{21}^3}{\pi^2c^3}$$

$$g_1B_{12} = g_2B_{21}$$

as expected.

(d) → If radiation is not black body these relations Still ~~not~~ hold, because Einstein coefficients are properties of the atom and their values are independent of the radiation field.

→ It is not necessary to assume only two levels because the principle of detailed balance requires ~~to~~ such relations to hold between any pair of levels. So in multi-level system we obtain the ~~exactly~~ same relations by applying ~~it to an~~ the principle to any pair of levels.

4. (a)

rate of stimulated transition equal to rate of spontaneous emission.

$$\cancel{N_2} B_{21} \rho(\omega_{21}) = \cancel{N_2} A_{21}$$

$$\rightarrow \frac{A_{21}}{B_{21}} = \rho(\omega_{21})$$

$$\because \frac{A_{21}}{B_{21}} = \frac{\hbar \omega_{21}^3}{\pi^2 c^3}$$

$$\therefore \frac{\hbar \omega_{21}^3}{\pi^2 c^3} = \rho(\omega_{21}) = \underbrace{\frac{\hbar \omega^3}{\pi^2 c^3} \left(\frac{1}{\exp(\frac{\hbar \omega_{21}}{k_B T}) - 1} \right)}_{\text{black body radiation}}$$

$$\rightarrow \frac{1}{\exp(\frac{\hbar \omega_{21}}{k_B T}) - 1} = 1 \rightarrow \exp\left(\frac{\hbar \omega_{21}}{k_B T}\right) = 2$$

$$\rightarrow k_B T = \frac{\hbar \omega_{21}}{\ln 2}$$

(b)

$$T = \left(\frac{\hbar}{k_B \ln 2}\right) \omega_{21}$$

$$\rightarrow \omega_{21} = 50 \text{ MHz} = \cancel{50} \; 2\pi \times 50 \times 10^6 \text{ Hz}$$

$$\rightarrow T = 0.0034 \text{ K}$$

$\rightarrow \omega_{21} = 2\pi \times 10^9 \, Hz$

$\rightarrow \underline{\underline{T = 0.069 \, K}}$ ✓

$\rightarrow \lambda = 500 \, nm \, , \quad \omega = \frac{2\pi c}{\lambda} = 3.77 \times 10^{15} \, Hz$

$\rightarrow \underline{\underline{T = 4.14 \times 10^4 \, K}}$ ✓

$\rightarrow \Delta E = 1 \, keV = 1000 \, eV$

$\omega = \frac{1000 \, eV}{\hbar} = 1.52 \times 10^{18} \, Hz$

$\rightarrow \underline{\underline{T = 1.67 \times 10^7 \, K}}$ ✓

5. (a) Atomic Hydrogen states are $|n \ell m\rangle$

n = principle quantum number
ℓ = angular momentum quantum number
m = magnetic quantum number.

For $n=1$, only state $|100\rangle$

~~transition~~ selection rule for ~~field~~ radiation polarised ~~in~~ along the z-axis is $\underline{\underline{\Delta m = 0}}$, $\underline{\underline{\Delta \ell = \pm 1}}$ ✓

$\therefore$ need $|100\rangle$ transition to $\underline{\underline{|210\rangle}}$

$\therefore$ Only $|210\rangle$ can be excited. ✓

(b) $\langle 1 | ez | 2 \rangle = e \langle 100 | z | 210 \rangle$

$$= e \int \langle 100 | r, \theta, \phi \rangle \langle r, \theta, \phi | z | r', \theta', \phi' \rangle \langle r', \theta', \phi' | 210 \rangle r^2 \sin\theta \, dr \, d\theta \, d\phi \; r'^2 \sin\theta' \, dr' \, d\theta' \, d\phi'$$

$$= e \int \langle 100 | r, \theta, \phi \rangle z \langle r', \theta', \phi' | 210 \rangle \underbrace{\langle r, \theta, \phi | r', \theta', \phi' \rangle}_{\delta^3(\underline{r})} r'^2 \sin\theta' \, dr' \, d\theta' \, d\phi' \; r^2 \sin\theta \, dr \, d\theta \, d\phi$$

$$= e \int \langle 100 | r, \theta, \phi \rangle \underbrace{z}_{\hookrightarrow r\cos\theta} \langle r, \theta, \phi | 210 \rangle r^2 \sin\theta \, dr \, d\theta \, d\phi$$

$$= e \int \underbrace{\left[\frac{2}{a_0^{3/2}} e^{-r/a_0} \right]}_{R_1^0} \underbrace{\left[r \cancel{\cos\theta} \right]}_{z \text{ term}} \underbrace{\left[\frac{1}{\sqrt{3}} \frac{1}{(2a_0)^{3/2}} \frac{1}{a_0} r e^{-r/2a_0} \right]}_{R_2^1} r^2 \, dr$$

$$\times \int \underbrace{\left[\sqrt{\frac{1}{4\pi}} \right]}_{Y_0^0} \underbrace{\left[\cos\theta \right]}_{z \text{ term}} \underbrace{\left[\sqrt{\frac{6}{8\pi}} \cos\theta \right]}_{Y_1^0} \sin\theta \, d\theta \, d\phi$$

$$= \frac{2e}{a_0^{3/2}} \frac{1}{\sqrt{3}} \frac{1}{\sqrt{8}} \frac{1}{a_0^{3/2}} \frac{1}{a_0} \sqrt{\frac{1}{4\pi}} \sqrt{\frac{6}{8\pi}} \int_0^\infty r^4 e^{-3r/2a_0} dr \int_0^{2\pi} d\phi \int_0^\pi \underbrace{\cos^2\theta \sin\theta}_{2/3}$$

$$= \frac{2e}{\pi a_0^4} \sqrt{\frac{\cancel{6}\ 1}{3\times 8\times 4\times 8\times 4}} \left(\int_0^\infty r^4 e^{-3r/2a_0} dr\right)(2\pi)\left(\frac{2}{3}\right)$$

$$= \frac{e}{\cancel{\pi} a_0^4} \frac{\cancel{2}}{\cancel{4}} \frac{1}{\cancel{8}\sqrt{2}} \cdot \cancel{2\pi} \cdot \frac{\cancel{2}}{3} \int_0^\infty r^4 e^{-3r/2a_0} dr$$

$$= \frac{e}{3\sqrt{2} a_0^4} \int_0^\infty \left(\frac{2a_0}{3}\right)^5 u^4 e^{-u} du$$

$$= \frac{e}{3\sqrt{2} a_0^4} \frac{2^5}{3^5} a_0^5 \int_0^\infty \underbrace{u^4 e^{-u} du}_{4!}$$

$u = \frac{3r}{2a_0}$

$du = \frac{3}{2a_0} dr$

$dr = \frac{2a_0}{3} du.$

$r^4 = \left(\frac{2a_0}{3}\right)^4 u^4$

$$= \boxed{\frac{128\sqrt{2}}{243} e a_0}$$

(c) The Einstein A coefficient

$$A_{21} = \frac{\omega^3 D_{12}^2}{3\pi c^3 \varepsilon_0 \hbar}$$

where $D_{12} = \langle 1 | ez | 2 \rangle = \frac{128\sqrt{2}}{243} e a_0 = 6.31 \times 10^{-30}$ C.m

$$\omega = \frac{E_2 - E_1}{\hbar} = (13.6\,eV)\left(\frac{1}{1^2} - \frac{1}{2^2}\right)\frac{1}{\hbar}$$

$$= 1.55 \times 10^{16}\ Hz$$

$$\rightarrow A_{21} = \frac{(1.55\times10^{16})^3(6.31\times10^{-30})^2}{3\pi(3.0\times10^8)^3(8.854\times10^{-12})(1.05\times10^{-34})}$$

$$= \cancel{6.26}\ \underline{\underline{6.27\times10^8\ s^{-1}}}$$

the lifetime of upper state is

$$\cancel{t=\frac{1}{A}}\quad \tau = \frac{1}{A_{21}} = \underline{\underline{1.60\times10^{-9}s}}$$

(d)

$$\text{poynting vector} \approx S \approx \cancel{1}\frac{1}{2\mu_0}EB \approx \frac{1}{2\mu_0}E\cdot\frac{E}{c}$$

$$= \frac{1}{2\mu_0 c}E^2$$

$$\text{Also}\quad S \approx \frac{\text{power}}{\text{area}} = \frac{P}{A} = \frac{1\times10^{-9}W}{\frac{\pi}{4}(0.001)^2 m^2} = 1.27\times10^{-3}\,W/m^2$$

$$\rightarrow 1.27\times10^{-3}\,W/m^2 \approx \frac{1}{2\mu_0 c}E^2$$

$\rightarrow$ Electric field ~~$E \approx \sqrt{\ldots\times10^{8}}\,V/m$~~ ~~$\ldots\times10^{4}\,N/C$~~ ~~$E \approx 0.692\,N/C$~~

$E = 0.978\,N/C$

The Rabi frequency

$$W_R \approx \frac{D_{12}E}{\hbar} = \frac{\langle100|ez|210\rangle E}{\hbar}$$

all going in the same direction.

$$= \frac{\frac{128\sqrt{2}}{243}a_0 E e}{\hbar} = \cancel{5.87}\ \boxed{5.87\times10^4\ \text{rad/s}}$$

$$\frac{1}{2}\epsilon_0 E^2 c = \frac{4\times10^{-9}}{\pi(10^{-3})^2} \rightarrow E \sim 1\,V/m$$

period of rabi oscillation

$$T_R = \frac{2\pi}{\omega_R} = 1.07 \times 10^{-4}$$

∵ ~~transitie~~

spontaneous transition lifetime $\tau = 1.6 \times 10^{-9}$ s

∴ $\tau \ll T_R$

The upper state electrons will decay long before one rabi oscillation is completed

→ No Rabi oscillation is observed.

6.

$$|\Psi(t)\rangle = C_1(t)\exp(-iE_1t/\hbar)|1\rangle + C_2(t)\exp(-iE_2t/\hbar)|2\rangle$$

where $\hat{H}|1\rangle = E_1|1\rangle$. $\hat{H}|2\rangle = E_2|2\rangle$

$$|C_1|^2 + |C_2|^2 = 1$$

Assume $\hat{V}(t) = e\underline{r}\cdot\underline{E_0}\cos(\omega t)$ $(\omega = \omega_0 + \delta)$

then let $\omega_1 = \frac{E_1}{\hbar}$, $\omega_2 = \frac{E_2}{\hbar}$, substitute everything into TDSE:

$(\hat{H} + \hat{V})|\Psi(t)\rangle = i\hbar\frac{\partial}{\partial t}|\Psi(t)\rangle$ gives

~~$\hat{H}|\Psi\rangle + e\underline{r}\cdot\underline{E_0}\cos(\omega t)|\Psi\rangle = i\hbar\frac{\partial\Psi\rangle}{\partial t}$~~

$$(\hat{H}+\hat{V})(C_1e^{-i\omega_1t}|1\rangle + C_2e^{-i\omega_2t}|2\rangle) = i\hbar\frac{\partial}{\partial t}(C_1e^{-i\omega_1t}|1\rangle + C_2e^{-i\omega_2t}|2\rangle)$$

$$\rightarrow \cancel{C_1e^{-i\omega_1t}E_1|1\rangle} + \cancel{C_2e^{-i\omega_2t}E_2|2\rangle} + C_1Ve^{-i\omega_1t}|1\rangle + C_2Ve^{-i\omega_2t}|2\rangle$$
$$= i\hbar\dot{C}_1e^{-i\omega_1t}|1\rangle + \cancel{\hbar C_1\omega_1e^{-i\omega_1t}|1\rangle} + i\hbar\dot{C}_2e^{-i\omega_2t}|2\rangle + \cancel{\hbar C_2\omega_2e^{-i\omega_2t}|2\rangle}$$

$$\rightarrow C_1Ve^{-i\omega_1t}|1\rangle + C_2Ve^{-i\omega_2t}|2\rangle$$
$$= i\hbar\dot{C}_1e^{-i\omega_1t}|1\rangle + i\hbar\dot{C}_2e^{-i\omega_2t}|2\rangle$$

$\langle 1|\cdot \Rightarrow$ $i\hbar\dot{C}_1e^{-i\omega_1t} = C_1e^{-i\omega_1t}\langle 1|V|1\rangle + C_2e^{-i\omega_2t}\langle 1|V|2\rangle$

$\because \omega_0 = \omega_2 - \omega_1 \rightarrow$ $\dot{C}_1 = -\frac{i}{\hbar}V_{11}C_1 - \frac{i}{\hbar}e^{-i\omega_0t}V_{12}C_2$

$\langle 2| \cdot \Rightarrow$

$$i\hbar \dot{c}_2 e^{-i\omega_2 t}|2\rangle = c_1 e^{-i\omega_1 t}\langle 2|V|1\rangle + c_2 e^{-i\omega_2 t}\langle 2|V|2\rangle$$

$$\rightarrow \quad \dot{c}_2 = -\frac{i}{\hbar}V_{21}c_1 e^{i\omega_0 t} - \frac{i}{\hbar}V_{22}c_2$$

$\because$ Atomic states have definite parity, and $V = e\underline{r}\cdot\underline{E_0}\cos\omega t = exE_0\cos\omega t$ (if $\underline{E_0} = E_0\hat{\underline{x}}$) has odd parity.

$\therefore$ $V_{11} = V_{22} = 0$ by their odd ~~sy~~ symmetry.

$\therefore$ we have

$$\boxed{\begin{aligned} \dot{c}_1 &= -\frac{i}{\hbar}V_{12}c_2 e^{-i\omega_0 t} \\ \dot{c}_2 &= -\frac{i}{\hbar}V_{21}c_1 e^{i\omega_0 t} \end{aligned}}$$

(b) $V = exE_0\cos(\omega t) = \frac{exE_0}{2}[\exp(i\omega t) + \exp(-i\omega t)]$

$$\Rightarrow \quad \dot{c}_1 = -\frac{i}{2\hbar}E_0\langle 1|ex|2\rangle\left[e^{i(\omega-\omega_0)t} + \cancel{\exp}\, e^{-i(\omega+\omega_0)t}\right]c_2$$

$$\dot{c}_2 = -\frac{i}{2\hbar}E_0\langle 1|ex|2\rangle\left[e^{-i(\omega-\omega_0)t} + e^{i(\omega+\omega_0)t}\right]c_1$$

($\langle 1|ex|2\rangle = \langle 2|ex|1\rangle$ because $|1\rangle, |2\rangle$ are real states, atomic states are real)

Rabi frequency $\Omega = \dfrac{\langle 1 | e x E_0 | 2 \rangle}{\hbar}$

$$\Rightarrow \quad \dot{c}_1 = -\frac{i}{2}\Omega\left[e^{i(\omega-\omega_0)t} + e^{-i(\omega+\omega_0)t}\right]c_2$$

$$\dot{c}_2 = -\frac{i}{2}\Omega\left[e^{-i(\omega-\omega_0)t} + e^{i(\omega_0+\omega)t}\right]c_1$$

→ Rotating wave approximation :

~~Assuming initially system in ground state.~~

~~$C_1(0)=1$ $\quad C_2(0)=0$~~

~~If perturbation $\hat{V}$ is weak we can assume that at later times most of the population still remains in the ground state.~~

rotating wave approximation is that when ~~$\omega+\omega_0$~~ $\omega-\omega_0 \ll \omega_0$, then we can neglect the $e^{\pm i(\omega+\omega_0)}$ terms in above differential equations. In this case $\omega = \omega_0 + \delta$ where $\delta \ll \omega_0$. When we integrate equations, the power of exponentials will be in the denominaters. so if $\delta \ll \omega_0$, then $\omega+\omega_0 \gg \omega-\omega_0$ $\therefore$ the term with $\omega+\omega_0$ can be neglected.

With this approximation the equations become.

$$\dot{c}_2 = -\frac{i}{2}\Omega c_1 \exp[-i\underbrace{(\omega-\omega_0)}_{\delta}t]$$

$$\dot{c}_1 = -\frac{i}{2}\Omega c_2 \exp[+i\underbrace{(\omega-\omega_0)}_{\delta}t]$$

$$\rightarrow \boxed{\begin{aligned} \dot{c}_2 &= -\tfrac{1}{2} i\Omega c_1 \exp(-it\delta) \quad (1) \\ \dot{c}_1 &= -\tfrac{1}{2} i\Omega c_2 \exp(+it\delta) \quad (2) \end{aligned}}$$

(c) $\frac{d(1)}{dt} \Rightarrow \ddot{c}_2 = -\frac{1}{2}i\Omega \dot{c}_1 \exp(-it\delta) - \frac{1}{2}i\Omega c_1 \exp(-it\delta)(-i\delta)$

$$\rightarrow \ddot{c}_2 = -\frac{1}{2}i\Omega\left(-\frac{1}{2}i\Omega c_2 \exp(\cancel{i\delta t})\right)\exp(\cancel{-i\delta t}) - i\delta \dot{c}_2$$

$$\cancel{-\frac{1}{2}i\Omega c_1(-i\delta)\exp} \quad \cancel{-i\delta \dot{c}_2}$$

$$\rightarrow \ddot{c}_2 + i\delta\dot{c}_2 = \frac{1}{4}(-1)\Omega^2 c_2 = -\frac{1}{4}\Omega^2 c_2$$

$$\rightarrow \ddot{c}_2 + i\delta c_2 + \frac{\Omega^2}{4}c_2 = 0$$

try $c_2 = A\exp(\Lambda t)$

$$\rightarrow \cancel{A^2 A + i\delta} \Rightarrow \Lambda^2 + i\delta\Lambda + \frac{\Omega^2}{4} = 0$$

$$\rightarrow \Lambda = \frac{-i\delta \pm \sqrt{-\delta^2-\Omega^2}}{2} = \frac{-i(\delta \pm \sqrt{\Omega^2+\delta^2})}{2}$$

Assumption for $V \Rightarrow$ dipole approximation

$\lambda \gg$ size of atom

$\therefore$ ~~$C_2 = A\exp(-\frac{i\delta}{2}t)$ exp~~

~~$C_2 = Ae^{-\frac{i\delta}{2}t}$~~

$$C_2 = A\exp(-\tfrac{i\delta}{2}t)\exp(-\tfrac{i}{2}\sqrt{\Omega^2+\delta^2}\,t)$$
$$+B\exp(-\tfrac{i\delta}{2}t)\exp(+\tfrac{i}{2}\sqrt{\Omega^2+\delta^2}\,t).$$
(general solution)

$\rightarrow$ If at $t=0$ ~~at~~ atom is in ground state $\Rightarrow$ ~~$C_2(t)=0$~~ $C_2(0)=0$
$C_1(0)=1$

then $0 = A+B \rightarrow B=-A$

$$\therefore \; C_2(t) = A\exp(-\tfrac{i\delta t}{2})\underbrace{\left(\exp(-\tfrac{i}{2}\sqrt{\Omega^2+\delta^2}\,t)-\exp(\tfrac{i}{2}\sqrt{\Omega^2+\delta^2}\,t)\right)}_{-2i\sin(\frac{1}{2}\sqrt{\Omega^2+\delta^2}\,t)}$$

$$= -2iA\exp(-\tfrac{i\delta t}{2})\sin(\tfrac{1}{2}t\sqrt{\Omega^2+\delta^2})$$

$$= A\exp(-\tfrac{i\delta t}{2})\sin(\tfrac{1}{2}t\sqrt{\Omega^2+\delta^2})$$

absorb all constants.

At $t=0$ $\quad C_1 = 1 \Rightarrow \dot{C}_2(0) = -\frac{1}{2}i\Omega$

$$\Rightarrow A(-\tfrac{i\delta}{2})\exp(-\tfrac{i\delta t}{2})\sin(\tfrac{1}{2}\sqrt{\Omega^2+\delta^2}\,t) + A\exp(-\tfrac{i\delta t}{2})\tfrac{1}{2}\sqrt{\Omega^2+\delta^2}\cos(\tfrac{1}{2}t\sqrt{\Omega^2+\delta^2})$$

$$= -\tfrac{1}{2}i\Omega \quad \text{at } t=0$$

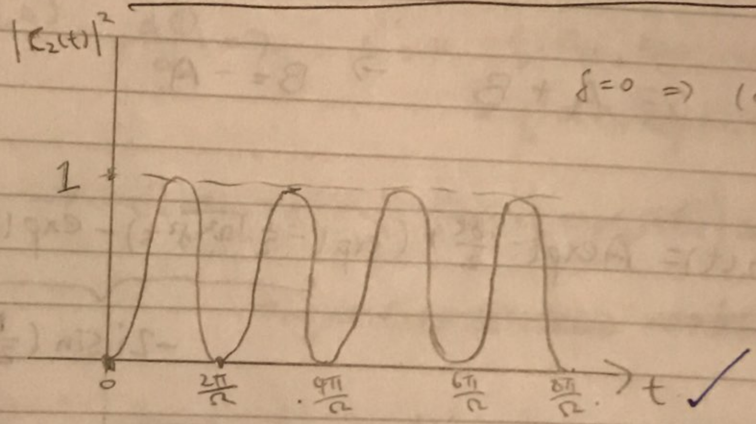
$$\rightarrow \quad A \cdot \frac{1}{2}\sqrt{\Omega^2+\delta^2} = -\frac{1}{2} i \Omega$$

$$\Rightarrow \quad A = \frac{-i\Omega}{\sqrt{\Omega^2+\delta^2}}$$

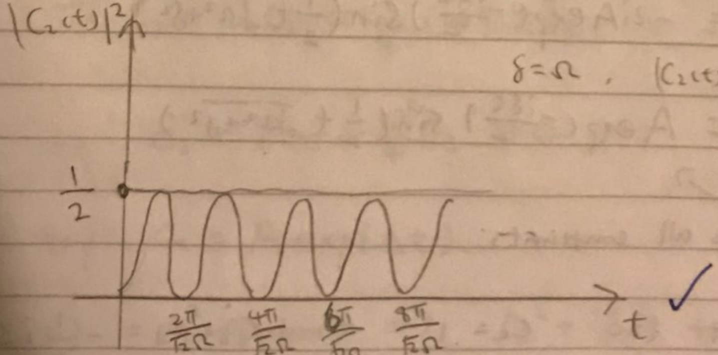
$$\Rightarrow \quad c_2(t) = -\frac{i\Omega}{\sqrt{\Omega^2+\delta^2}} \exp\left(-\frac{i\delta}{2}t\right) \sin\left(\frac{1}{2}t\sqrt{\Omega^2+\delta^2}\right)$$

$$\Rightarrow \quad |c_2(t)|^2 = \frac{\Omega^2}{\Omega^2+\delta^2} \sin^2\left(\frac{1}{2}t\sqrt{\Omega^2+\delta^2}\right)$$

$\delta = 0 \Rightarrow |c_2(t)|^2 = \sin^2\left(\frac{1}{2}\Omega t\right)$



$\delta = \Omega, \quad |c_2(t)|^2 = \frac{1}{2}\sin^2\left(\frac{\sqrt{2}}{2}\Omega t\right)$



7. (a) resonant driving $\delta = 0$

$$\dot{c}_2 = -\frac{i}{2}\Omega c_1 \qquad \text{At } t=0 \quad c_2 = 0$$

$$\dot{c}_1 = -\frac{i}{2}\Omega c_2 \qquad\qquad c_1 = 1$$

$$\rightarrow \quad \ddot{c}_2 = -\frac{i}{2}\Omega \dot{c}_1 = -\frac{i}{2}\Omega\left(-\frac{i}{2}\Omega c_2\right)$$

$$= -\frac{1}{4}\Omega^2 c_2$$

$$\rightarrow \quad \ddot{c}_2 + \frac{\Omega^2}{4} c_2 = 0$$

$$\rightarrow \quad c_2 = A\cos\left(\frac{\Omega}{2}t\right) + B\sin\left(\frac{\Omega}{2}t\right)$$

At $t=0$ $\quad c_2 = 0 \quad \Rightarrow \quad A = 0$

$$\rightarrow \quad c_2 = B\sin\left(\frac{\Omega}{2}t\right)$$

At $t=0$ $\quad c_1 = 1 \quad \Rightarrow \quad \dot{c}_2(0) = -\frac{i}{2}\Omega$

$$\therefore \quad \frac{1}{2}\cancel{\Omega} B\cos(\Omega/2\,(t))\Big|_{t=0} = -\frac{i}{2}\cancel{\Omega}.$$

$$\Rightarrow \quad B = -i$$

$$\Rightarrow \quad c_2 = -i\sin\left(\frac{\Omega}{2}t\right).$$

$$\dot{c}_2 = -\frac{i}{2}\Omega\cos\left(\frac{\Omega}{2}t\right)$$

$$\therefore \quad c_1 = -\frac{2}{i\Omega}\dot{c}_2 = -\frac{2}{i\Omega}\,\frac{-i}{2}\Omega = +\cos\left(\frac{\Omega}{2}t\right) ✓$$

$\rightarrow$

$$\Rightarrow \boxed{\begin{cases} C_1 = \cos(\frac{\Omega}{2}t) \\ C_2 = -i\sin(\frac{\Omega}{2}t) \end{cases}}$$

(b)

$$|\psi(t)\rangle = C_1 \exp(-iE_1 t/\hbar)|1\rangle + C_2 \exp(-\frac{iE_2 t}{\hbar})|2\rangle$$

$\rightarrow$ if $t = \frac{\pi}{2\Omega}$: , $C_1 = \cos(\frac{\pi}{4}) = \frac{\sqrt{2}}{2}$

$C_2 = i\sin(\frac{\pi}{4}) = -i\frac{\sqrt{2}}{2}$

$$\therefore |\psi(t)\rangle = \frac{1}{\sqrt{2}}\left(\exp(-\frac{iE_1\pi}{2\Omega\hbar})|1\rangle - i\exp(-\frac{iE_2\pi}{2\Omega\hbar})|2\rangle\right)$$

$|\psi\rangle = \frac{1}{\sqrt{2}}(|1\rangle - i|2\rangle) \propto |1\rangle - i|2\rangle$

$\rightarrow$ if $t = \frac{\pi}{\Omega}$, $C_1 = \cos(\frac{\pi}{2}) = 0$

$C_2 = -i\sin(\frac{\pi}{2}) = -i$

$\therefore$ ~~$|\psi(t)\rangle =$~~

$|\psi\rangle = -i|2\rangle$

$\rightarrow$ if $t = \frac{2\pi}{\Omega}$, $C_1 = \cos(\pi) = -1$

$C_2 = -i\sin(\pi) = 0$

$\rightarrow$ $|\psi\rangle = -|1\rangle$

(c)

In Bloch representation

$$c_1 = \sin(\theta/2)$$
$$c_2 = e^{i\phi}\cos(\theta/2)$$

maps (c_1, c_2) to (θ, ϕ) or vice versa.

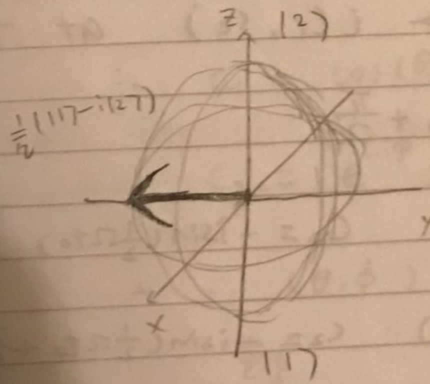
$\to$ $t = \frac{\pi}{2\Omega}$, $c_1 = \frac{\sqrt{2}}{2}$, $c_2 = -i\frac{\sqrt{2}}{2}$

$\to$ $c_1 = \frac{\sqrt{2}}{2} = \sin(\frac{\theta}{2}) \to \theta = \frac{\pi}{2}$

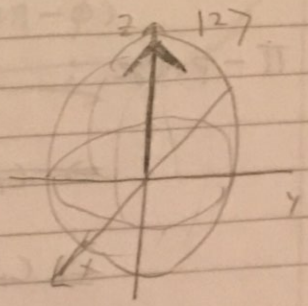
$c_2 = e^{i\phi}\underbrace{\cos(\frac{\pi}{4})}_{\frac{\sqrt{2}}{2}} = \cancel{\frac{\sqrt{2}}{2}} - i\frac{\sqrt{2}}{2} \to e^{i\phi} = -i$

$\to \phi = \frac{3\pi}{2}$

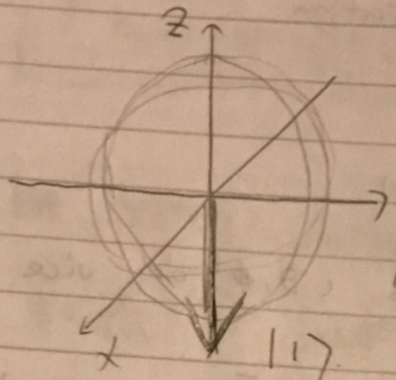
$\therefore (\theta, \phi) = (\frac{\pi}{2}, \frac{3\pi}{2})$



$\to$ $t = \frac{\pi}{\Omega}$, $c_1 = 0$ $c_2 = 1$



→ $t = \frac{2\pi}{\Omega}$ $\quad c_1 = 1 \quad c_2 = 0$



the axis of rotation is the x-axis

$(x, y, z) = \underline{\underline{(1, 0, 0)}}$ ✓

(d) a general state after a π-pulse :

→ state ~~c_1, c_2 $|\psi_0\rangle$~~ (c_1, c_2) at t_0

After π-pulse $t_\pi = t_0 + \frac{\pi}{\Omega}$

$\therefore$ $c_1 = \cos(\frac{1}{2}\Omega t_0)$ $\quad c_2 = -i\sin(\frac{1}{2}\Omega t_0)$

π-pulse : $c_1' = \cos(\frac{1}{2}\Omega t_0 + \frac{\pi}{2})$ $\quad c_2 = -i\sin(\frac{1}{2}\Omega t_0 + \frac{\pi}{2})$

~~→ $c_1' = -i\sin(\frac{1}{2}\Omega t_0)$; $c_2' = \cos(\frac{1}{2}\Omega t_0)$~~

→ $c_1' = i c_2$ ~~$c_2' = c_1$~~

$c_1' = -\sin(\frac{1}{2}\Omega t_0) = -i c_2$

$c_2' = -i\cos(\frac{1}{2}\Omega t_0) = -i c_1$

$(c_1, c_2) \to (-ic_2, -ic_1)$ after π-pulse

∵ $c_1 = \sin(\theta/2)$, $c_2 = e^{i\phi}\cos(\theta/2)$

$\cancel{\therefore\ c_1' = -ic_2 = -ie^{i\phi}\cos(\theta/2) = e^{i(\phi-\frac{\pi}{2})}\sin(\frac{\theta-\pi}{2})}$

$\cancel{c_2' = -ic_1 = e^{i}}$

$\cancel{\therefore\ (c_1', c_2') \propto (c_1, c_2)}$

$\cancel{c_1' = \cos(\theta/2)}$

$c_1' = -ic_2 = -ie^{i\phi}\cos(\theta/2)$

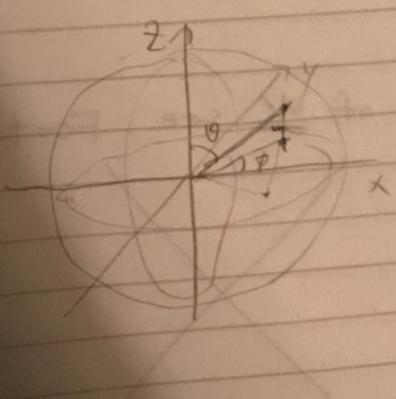
$c_2' = -ic_1 = -i\sin(\theta/2)$

→ turn c_1' into real and positive : divide both by $-ie^{i\phi}$

∴ $c_1' = \cos(\theta/2) = \sin(\frac{\pi-\theta}{2})$

$c_2' = e^{-i\phi}\sin(\theta/2) = e^{i(2\pi-\phi)}\cos(\frac{\pi-\theta}{2})$

∴ $(\theta, \phi) \to (\pi-\theta, 2\pi-\phi)$ ✓



→ This is still ~~a~~ a rotation about the x-axis ✓

(because along x-axis ~~interg~~ interchange c_1 and c_2 leaves state invariant up to a constant 1 or −1)

To perform an rotation ~~⊥~~ orthogonal to the x-axis ~~I~~ need the rotation axis

$\underline{W} = \Omega \hat{\underline{x}} + \delta \hat{\underline{z}}$ to be along $\hat{\underline{z}}$

→ $\Omega = 0$

~~then~~ → $\dot{c}_2 = 0$

$\dot{c}_1 = 0$

at all times

~~states~~ there is ~~not~~ no rotation because the state $|\psi\rangle = c_1|1\rangle + c_2|2\rangle$ is not changing

→ $\boxed{\text{impossible}}$

(derivation of the form of $\underline{W}$ see Foot pp 128-131)

stupid!

(correction)

So ~~ex~~ rotation about z direction is impossible.

What about rotation about y-direction ?

→ It is possible if the laser is a "sine" laser rather than a "cosine" laser.

Everything is the same up to.

$$\dot{c}_1 = -\frac{i}{\hbar} V_{12} c_2 e^{-i\omega_0 t}$$

$$\dot{c}_2 = -\frac{i}{\hbar} V_{12} c_1 e^{i\omega_0 t}$$

But now $V = exE_0 \sin(\omega t)$

$$= \frac{exE}{2i}[\exp(i\omega t) - \exp(-i\omega t)]$$

$$\rightarrow \dot{c}_1 = -\frac{i}{\hbar}\left(\frac{eE}{2i}\right)\langle 1|x|2\rangle c_2 \left[e^{i(\omega-\omega_0)t} - e^{-i(\omega+\omega_0)t}\right]$$

$$\dot{c}_2 = -\frac{i}{\hbar}\left(\frac{eE}{2i}\right)\langle 1|x|2\rangle \left[e^{i(\omega+\omega_0)t} - e^{-i(\omega-\omega_0)t}\right] c_1$$

Rotating wave approximation : $(\delta = \omega - \omega_0)$ $\left(\Omega = \frac{\langle 1|exE_0|2\rangle}{\hbar}\right)$

$$\dot{c}_1 = -\frac{1}{2}\Omega e^{i\delta t} c_2$$

$$\dot{c}_2 = +\frac{1}{2}\Omega e^{-i\delta t} c_1$$

(correction)

Resonant driving $\delta = 0$

$\rightarrow \quad \dot{c}_1 = -\frac{1}{2}\Omega c_2$

$\dot{c}_2 = \frac{1}{2}\Omega c_1$

$\ddot{c}_2 = \frac{1}{2}\Omega \dot{c}_1 = -\frac{1}{4}\Omega^2 c_2$

$\Rightarrow \quad \ddot{c}_2 + \frac{\Omega^2}{4} c_2 = 0 \rightarrow c_2 = A\cos\left(\frac{\Omega}{2}t\right) + B\sin\left(\frac{\Omega}{2}t\right)$

At $t=0$, $c_2 = 0 \Rightarrow A = 0$

$\therefore \quad c_2 = B\sin\left(\frac{\Omega}{2}t\right)$

At $t=0$, $c_1 = 1 \Rightarrow \dot{c}_2(0) = \frac{1}{2}\Omega$

$\therefore \quad \frac{1}{2}\Omega B \cos\left(\frac{\Omega}{2}t\right)\Big|_{t=0} = \frac{1}{2}\Omega$

$\therefore B = 1 \quad \therefore \quad c_2 = \sin\left(\frac{\Omega}{2}t\right)$

$c_1 = \frac{2}{\Omega}\dot{c}_2 = \frac{2}{\Omega}\cdot\frac{\Omega}{2}\cos\left(\frac{\Omega}{2}t\right) = \cos\left(\frac{\Omega}{2}t\right)$

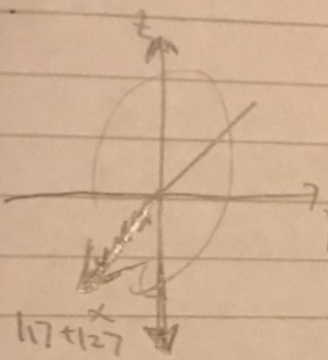
$$\therefore \quad \boxed{\begin{cases} c_1 = \cos\left(\frac{\Omega}{2}t\right) \\ c_2 = \sin\left(\frac{\Omega}{2}t\right) \end{cases}}$$

Starting from state $|1\rangle$ at $t=0$

(correction)

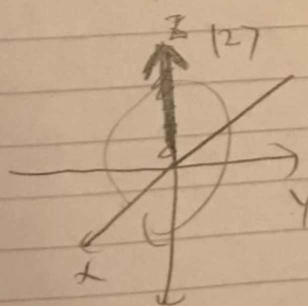
At $t=\frac{\pi}{2\Omega}$: $c_1=\frac{\sqrt{2}}{2}$, $c_2=\frac{\sqrt{2}}{2}$

$\therefore \quad |\psi\rangle \propto |1\rangle+|2\rangle$



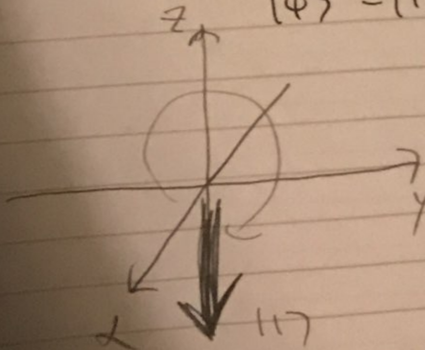
At $t=\frac{\pi}{\Omega}$, $c_1=0$ $c_2=1$

$|\psi\rangle=|2\rangle$



At $t=\frac{2\pi}{\Omega}$: $c_1=1$ $c_2=0$.

$|\psi\rangle=|1\rangle$



$\Rightarrow$ This is a rotation about x-direction.

$\rightarrow$ $\boxed{\text{Possible}}$

Problem Set 3

Molecules and radiative transitions

Some questions require further reading or looking up of facts, but many answers can be found in the lecture notes. They should be written out nevertheless - important derivations and proofs need to be worked through. The questions have been chosen to cover the ground as economically as possible, so there is little repetition. Starred problems (*) are more challenging and may be omitted initially.

1. (a) Suppose that the valence electrons of the molecule are confined to a region of size a. Show that the electronic energy of the molecule will be of order,

$$E_e = \frac{\hbar^2}{2ma^2}$$

where m is the electron mass.

(b) Show that the vibrational energy of the molecule will be of the order,

$$E_v \approx \hbar\omega_v \approx \sqrt{\frac{m}{\mu}} E_e,$$

where $\mu = M_1 M_2/(M_1 + M_2)$ is the reduced mass of the two nuclei. Find an expression for the vibrational frequency ω_v in terms of a and μ.

(c) Show that the rotational energy of the molecule will be of order,

$$E_r = \frac{m}{\mu} E_e.$$

(d) For the HCl molecule the equilibrium separation is $R_0 = 0.128\,\mathrm{nm}$. Construct a table giving the energy scale, characteristic frequency, and characteristic timescale of the electronic, vibrational, and rotational motions.

(e) A quantum treatment shows that the energy levels of diatomic molecules may be written in the form,

$$E = E_e + (v + 1/2)\hbar\omega_v + B_r K(K+1).$$

Use your results to find approximate values for ω_v and B_r, and compare these with the measured values of $\tilde{\nu}_v = \omega_v/2\pi c = 2090\,\mathrm{cm}^{-1}$ and $B_r = 20.8\,\mathrm{cm}^{-1}$.

2*. The interaction potential for a diatomic molecule is parametrized using the Morse potential:

$$V(r) = D\left[1 - e^{-\beta(r-r_0)}\right]^2,$$

where r_0 is the equilibrium nuclear separation, and D and β are constants.

(a) Treating the diatomic molecule as a classical harmonic oscillator, derive the vibrational frequency, ω_v, in terms of the Morse potential parameters and the reduced mass of the system (μ).

(b) Now suppose the molecule is rotating. The induced perturbation in the interatomic potential can be modelled in terms of an effective potential

$$V_{eff}(r) = D\left[1 - e^{-\beta(r-r_0)}\right]^2 + \frac{\hbar^2 K(K+1)}{2\mu r^2},$$

where K is the rotational quantum number. Determine the new equilibrium distance between the two atoms.

(c) Show that this change in separation leads to a new term in the molecular energy of the form $\Delta E = -B_1 K^2 (K+1)^2$, where

$$B_1 = \frac{8}{\hbar^2 \omega_v^2} \left(\frac{\hbar^2}{2\mu r_0^2} \right)^3 .$$

3. (a) Assume that transitions between two levels in an atom occur only by radiative processes (namely stimulated emission or absorption, and spontaneous emission). Show that the ratio of the steady-state populations is

$$\frac{N_2}{N_1} = \frac{B_{12}\rho(\omega_{21})}{B_{21}\rho(\omega_{21}) + A_{21}}$$

where $\rho(\omega)$ is the energy density per unit (angular) frequency of the radiation field driving the stimulated processes, ω_{21} is the transition frequency, and A and B are the Einstein coefficients.

(b) What happens to the relative populations in the two levels as the energy density of the radiation is increased to very large values? Would it be possible to create a population inversion this way?

(c) In thermal equilibrium, the radiation density is given by the Planck black-body distribution. Show that this leads to the following relations between the Einstein coefficients:

$$B_{21} = \frac{g_1}{g_2} B_{12} \qquad A_{21} = \frac{\hbar \omega_{21}^3}{\pi^2 c^3} B_{21}$$

where g_1 and g_2 are the degeneracies of the lower and upper levels.

(d) Does the relation between A_{21} and B_{21} still hold if the radiation is *not* black-body? Is it necessary to assume that the atom has *only* two levels?

4. A blob of matter is placed in a cavity and allowed to interact with blackbody radiation of temperature T. (a) Show that for a transition of angular frequency ω_{21}, the rate of stimulated emission becomes equal to that of spontaneous emission when

$$k_B T = \frac{\hbar \omega_{21}}{\ln 2}$$

(b) Calculate this temperature for the following transitions:

- radio frequencies of 50 MHz
- microwaves at 1 GHz
- visible light of wavelength 500 nm
- X-rays of energy 1 keV

$$\frac{\cancel{\pi} e^2 D_{12}^2}{3\epsilon_0 \hbar^{\cancel{2}}} \cdot \frac{\cancel{\hbar}\omega_{21}^3}{\pi^{\cancel{2}} c^3}$$

5. (a) Atomic hydrogen is illuminated by light resonant with the $n = 1 \rightarrow n = 2$ Lyman-α transition, linearly polarized along the z-axis. Which upper state(s) can be excited?

$$\frac{\omega_{21}^3 e^2 D_{12}^2}{3\pi c^3 \epsilon_0 \hbar}$$

$\frac{1}{2\mu_0 c} E^2 = I$

$\frac{1}{\mu_0} = c\epsilon$

(b) Calculate the electric dipole matrix element $\langle 1|ez|2\rangle$ for the transition, expressing your answer in units of ea_0 where a_0 is the Bohr radius. (Look up the relevant hydrogen wavefunctions.)

(c) Use your result to calculate the Einstein A coefficient for the transition, and hence the lifetime of the upper state.

(d) A laser capable of producing continuous wave Lyman-α radiation was recently developed, which yielded a power of 1 nW in a beam of 1 mm diameter. Estimate the Rabi frequency if the laser were tuned to resonance with this transition. Comment on the feasibility of observing Rabi oscillations in this system.

6. (a) A two-level atom has eigenstates $|1\rangle$ and $|2\rangle$ of a time-independent Hamiltonian $\hat{H}$ which are separated by an energy $\hbar\omega_0 = E_2 - E_1$. Monochromatic light of amplitude $\mathbf{E}_0$ and angular frequency $\omega = \omega_0 + \delta$ (where $\delta \ll \omega_0$) is incident on the atom. Writing the wavefunction as

$$|\Psi(t)\rangle = c_1(t)\exp(-\imath E_1 t/\hbar)|1\rangle + c_2(t)\exp(-\imath E_2 t/\hbar)|2\rangle$$

show by substitution into the time-dependent Schrödinger equation, with Hamiltonian $\hat{H} + \hat{V}(t)$, that the rate of change of the coefficient c_2 is

$$\dot{c}_2 = -\frac{\imath}{\hbar} V_{21} c_1 \exp(\imath\omega_0 t)$$

where $V_{21} = V_{12} = \langle 1|\hat{V}|2\rangle = \langle 1|e\mathbf{r}.\mathbf{E}_0|2\rangle \cos\omega t$ and $V_{11} = V_{22} = 0$. What assumptions have you made about the "perturbation" $\hat{V}$?

(b) Explain what is meant by the *rotating wave approximation* and justify its use here. Make it, and show that this leads to the following coupled differential equations for the coefficients:

$$\dot{c}_2 = -\tfrac{1}{2}\imath\Omega c_1 \exp(-\imath t\delta)$$
$$\dot{c}_1 = -\tfrac{1}{2}\imath\Omega c_2 \exp(+\imath t\delta)$$

where the Rabi frequency $\Omega = \langle 1|e\mathbf{r}.\mathbf{E}_0|2\rangle/\hbar$.

(c) Solve for $c_2(t)$ and hence show that, if the atom is in state $|1\rangle$ at $t = 0$, the probability of finding it in state $|2\rangle$ at later time t is given by

$$|c_2(t)|^2 = \frac{\Omega^2}{\Omega^2 + \delta^2}\sin^2\left(\tfrac{1}{2}t\sqrt{\Omega^2 + \delta^2}\right)$$

Sketch this probability as a function of time for the cases $\delta = 0$ and $\delta = \Omega$.

7*. (a) Find the solutions $c_1(t)$ and $c_2(t)$ to the differential equations in the previous question, with the same initial conditions, but for the case of resonant driving ($\delta = 0$).

(b) What is the state of the system after times given by $\Omega t = \pi/2, \pi, 2\pi$?

(c) Sketch the positions of the Bloch vector at these times, with the convention that the angular co-ordinates (θ, ϕ) on the Bloch sphere are defined by $c_1 = \sin\left(\frac{\theta}{2}\right)$ and $c_2 = e^{\imath\phi}\cos\left(\frac{\theta}{2}\right)$. Which axis (x, y, z) is the rotation around?

(d) What happens to a general state at co-ordinates (θ, ϕ) after a π-pulse (that is, after a time $t = \pi/\Omega$)? Is this a rotation about the same axis? Is it possible to perform a rotation about an axis orthogonal to this one?