Chapter 9

Time-Dependent Perturbation Theory

Problem 9.1

$\psi_{nlm} = R_{nl}Y_l^m$. From Tables 4.3 and 4.7:

$$\psi_{100} = \frac{1}{\sqrt{\pi a^3}}e^{-r/a}; \quad \psi_{200} = \frac{1}{\sqrt{8\pi a^3}}\left(1 - \frac{r}{2a}\right)e^{-r/2a};$$

$$\psi_{210} = \frac{1}{\sqrt{32\pi a^3}}\frac{r}{a}e^{-r/2a}\cos\theta; \quad \psi_{21\pm1} = \mp\frac{1}{\sqrt{64\pi a^3}}\frac{r}{a}e^{r/2a}\sin\theta\, e^{\pm i\phi}.$$

But $r\cos\theta = z$ and $r\sin\theta e^{\pm i\phi} = r\sin\theta(\cos\phi \pm i\sin\phi) = r\sin\theta\cos\phi \pm ir\sin\theta\sin\phi = x \pm iy$. So $|\psi|^2$ is an *even* function of z in all cases, and hence $\int z|\psi|^2 dx\, dy\, dz = 0$, so $\boxed{H'_{ii} = 0.}$ Moreover, ψ_{100} is even in z, and so are ψ_{200}, ψ_{211}, and ψ_{21-1}, so $\boxed{H'_{ij} = 0}$ for all *except*

$$H'_{100,210} = -eE\frac{1}{\sqrt{\pi a^3}}\frac{1}{\sqrt{32\pi a^3}}\frac{1}{a}\int e^{-r/a}e^{-r/2a}z^2\, d^3\mathbf{r} = -\frac{eE}{4\sqrt{2}\pi a^4}\int e^{-3r/2a}r^2\cos^2\theta\, r^2\sin\theta\, dr\, d\theta\, d\phi$$

$$= -\frac{eE}{4\sqrt{2}\pi a^4}\int_0^\infty r^4e^{-3r/2a}dr\int_0^\pi \cos^2\theta\sin\theta\, d\theta\int_0^{2\pi} d\phi = -\frac{eE}{4\sqrt{2}\pi a^4}4!\left(\frac{2a}{3}\right)^5\frac{2}{3}2\pi = \boxed{-\left(\frac{2^8}{3^5\sqrt{2}}\right)eEa,}$$

or $\boxed{-0.7449\, eEa.}$

Problem 9.2

$$\dot{c}_a = -\frac{i}{\hbar}H'_{ab}e^{-i\omega_0 t}c_b; \quad \dot{c}_b = -\frac{i}{\hbar}H'_{ba}e^{i\omega_0 t}c_a. \quad \text{Differentiating with respect to } t:$$

$$\ddot{c}_b = -\frac{i}{\hbar}H'_{ba}\left[i\omega_0 e^{i\omega_0 t}c_a + e^{i\omega_0 t}\dot{c}_a\right] = i\omega_0\left[-\frac{i}{\hbar}H'_{ba}e^{i\omega_0 t}c_a\right] - \frac{i}{\hbar}H'_{ba}e^{i\omega_o t}\left[-\frac{i}{\hbar}H'_{ab}e^{-i\omega_0 t}c_b\right], \text{ or}$$

$$\ddot{c}_b = i\omega_0\dot{c}_b - \frac{1}{\hbar^2}|H'_{ab}|^2 c_b. \quad \text{Let} \quad \alpha^2 \equiv \frac{1}{\hbar^2}|H'_{ab}|^2. \quad \text{Then} \quad \ddot{c}_b - i\omega_0\dot{c}_b + \alpha^2 c_b = 0.$$

This is a linear differential equation with constant coefficients, so it can be solved by a function of the form $c_b = e^{\lambda t}$:

$$\lambda^2 - i\omega_0\lambda + \alpha^2 = 0 \Longrightarrow \lambda = \frac{1}{2}\left[i\omega_0 \pm \sqrt{-\omega_0^2 - 4\alpha^2}\right] = \frac{i}{2}(\omega_0 \pm \omega), \text{ where } \omega \equiv \sqrt{\omega_0^2 + 4\alpha^2}.$$

The general solution is therefore

$$c_b(t) = Ae^{i(\omega_0+\omega)/2} + Be^{i(\omega_0-\omega)/2} = e^{i\omega_0 t/2}\left(Ae^{i\omega t/2} + Be^{-i\omega t/2}\right), \text{ or}$$

$$c_b(t) = e^{i\omega_0 t/2}\left[C\cos(\omega t/2) + D\sin(\omega t/2)\right]. \quad \text{But} \quad c_b(0) = 0, \quad \text{so} \quad C = 0, \quad \text{and hence}$$

$$c_b(t) = De^{i\omega_0 t/2}\sin(\omega t/2). \quad \text{Then}$$

$$\dot{c}_b = D\left[\frac{i\omega_0}{2}e^{i\omega_0 t/2}\sin(\omega t/2) + \frac{\omega}{2}e^{i\omega_0 t/2}\cos(\omega t/2)\right] = \frac{\omega}{2}De^{i\omega_0 t/2}\left[\cos(\omega t/2) + i\frac{\omega_0}{\omega}\sin(\omega t/2)\right] = -\frac{i}{\hbar}H'_{ba}e^{i\omega_0 t}c_a.$$

$$c_a = \frac{i\hbar}{H'_{ba}}\frac{\omega}{2}e^{-i\omega_0 t/2}D\left[\cos(\omega t/2) + i\frac{\omega_0}{\omega}\sin(\omega t/2)\right]. \quad \text{But} \quad c_a(0) = 1, \quad \text{so} \quad \frac{i\hbar}{H'_{ba}}\frac{\omega}{2}D = 1. \quad \textit{Conclusion:}$$

$$\boxed{\begin{aligned} c_a(t) &= e^{-i\omega_0 t/2}\left[\cos(\omega t/2) + i\frac{\omega_0}{\omega}\sin(\omega t/2)\right], \\ c_b(t) &= \frac{2H'_{ba}}{i\hbar\omega}e^{i\omega_0 t/2}\sin(\omega t/2), \end{aligned}} \quad \text{where} \quad \boxed{\omega \equiv \sqrt{\omega_0^2 + 4\frac{|H'_{ab}|^2}{\hbar^2}}.}$$

$$\begin{aligned} |c_a|^2 + |c_b|^2 &= \cos^2(\omega t/2) + \frac{\omega_0^2}{\omega^2}\sin^2(\omega t/2) + \frac{4|H'_{ab}|^2}{\hbar^2\omega^2}\sin^2(\omega t/2) \\ &= \cos^2(\omega t/2) + \frac{1}{\omega^2}\left(\omega_0^2 + 4\frac{|H'_{ab}|^2}{\hbar^2}\right)\sin^2(\omega t/2) = \cos^2(\omega t/2) + \sin^2(\omega t/2) = 1. \quad \checkmark \end{aligned}$$

Problem 9.3

This is a tricky problem, and I thank Prof. Onuttom Narayan for showing me the correct solution. The safest approach is to represent the delta function as a sequence of rectangles:

$$\delta_\epsilon(t) = \left\{\begin{array}{ll} (1/2\epsilon), & -\epsilon < t < \epsilon, \\ 0, & \text{otherwise.} \end{array}\right\}$$

Then Eq. 9.13 $\Rightarrow$

$$\begin{cases} t < -\epsilon: & c_a(t) = 1,\ c_b(t) = 0, \\ t > \epsilon: & c_a(t) = a,\ c_b(t) = b, \\ -\epsilon < t < \epsilon: & \begin{cases} \dot{c}_a = -\frac{i\alpha}{2\epsilon\hbar}e^{-i\omega_0 t}c_b, \\ \dot{c}_b = -\frac{i\alpha^*}{2\epsilon\hbar}e^{i\omega_0 t}c_a. \end{cases} \end{cases}$$

In the interval $-\epsilon < t < \epsilon$,

$$\frac{d^2c_b}{dt^2} = -\frac{i\alpha^*}{2\epsilon\hbar}\left[i\omega_0 e^{i\omega_0 t}c_a + e^{i\omega_0 t}\left(\frac{-i\alpha}{2\epsilon\hbar}e^{-i\omega_0 t}c_b\right)\right] = -\frac{i\alpha^*}{2\epsilon\hbar}\left[i\omega_0\frac{i2\epsilon\hbar}{\alpha^*}\frac{dc_b}{dt} - \frac{i\alpha}{2\epsilon\hbar}c_b\right] = i\omega_0\frac{dc_b}{dt} - \frac{|\alpha|^2}{(2\epsilon\hbar)^2}c_b.$$

Thus c_b satisfies a homogeneous linear differential equation with constant coefficients:

$$\frac{d^2c_b}{dt^2} - i\omega_0\frac{dc_b}{dt} + \frac{|\alpha|^2}{(2\epsilon\hbar)^2}c_b = 0.$$

Try a solution of the form $c_b(t) = e^{\lambda t}$:

$$\lambda^2 - i\omega_0\lambda + \frac{|\alpha|^2}{(2\epsilon\hbar)^2} = 0 \Rightarrow \lambda = \frac{i\omega_0 \pm \sqrt{-\omega_0^2 - |\alpha|^2/(\epsilon\hbar)^2}}{2},$$

or

$$\lambda = \frac{i\omega_0}{2} \pm \frac{i\omega}{2}, \text{ where } \omega \equiv \sqrt{\omega_0^2 + |\alpha|^2/(\epsilon\hbar)^2}.$$

The general solution is

$$c_b(t) = e^{i\omega_0 t/2}\left(Ae^{i\omega t/2} + Be^{-i\omega t/2}\right).$$

But

$$c_b(-\epsilon) = 0 \Rightarrow Ae^{-i\omega\epsilon/2} + Be^{i\omega\epsilon/2} = 0 \Rightarrow B = -Ae^{-i\omega\epsilon},$$

so

$$c_b(t) = Ae^{i\omega_0 t/2}\left(e^{i\omega t/2} - e^{-i\omega(\epsilon+t/2)}\right).$$

Meanwhile

$$\begin{aligned} c_a(t) &= \frac{2i\epsilon\hbar}{\alpha^*}e^{-i\omega_0 t}\dot{c}_b = \frac{2i\epsilon\hbar}{\alpha^*}e^{-i\omega_0 t/2}A\left[\frac{i\omega_0}{2}\left(e^{i\omega t/2} - e^{-i\omega(\epsilon+t/2)}\right) + \frac{i\omega}{2}\left(e^{i\omega t/2} + e^{-i\omega(\epsilon+t/2)}\right)\right] \\ &= -\frac{\epsilon\hbar}{\alpha^*}e^{-i\omega_0 t/2}A\left[(\omega+\omega_0)e^{i\omega t/2} + (\omega-\omega_0)e^{-i\omega(\epsilon+t/2)}\right]. \end{aligned}$$

But $\quad c_a(-\epsilon) = 1 = -\dfrac{\epsilon\hbar}{\alpha^*}e^{i(\omega_0-\omega)\epsilon/2}A\left[(\omega+\omega_0) + (\omega-\omega_0)\right] = -\dfrac{2\epsilon\hbar\omega}{\alpha^*}e^{i(\omega_0-\omega)\epsilon/2}A, \quad$ so $\quad A = -\dfrac{\alpha^*}{2\epsilon\hbar\omega}e^{i(\omega-\omega_0)\epsilon/2}.$

$$\begin{aligned} c_a(t) &= \frac{1}{2\omega}e^{-i\omega_0(t+\epsilon)/2}\left[(\omega+\omega_0)e^{i\omega(t+\epsilon)/2} + (\omega-\omega_0)e^{-i\omega(t+\epsilon)/2}\right] \\ &= e^{-i\omega_0(t+\epsilon)/2}\left\{\cos\left[\frac{\omega(t+\epsilon)}{2}\right] + i\frac{\omega_0}{\omega}\sin\left[\frac{\omega(t+\epsilon)}{2}\right]\right\}; \\ c_b(t) &= -\frac{i\alpha^*}{2\epsilon\hbar\omega}e^{i\omega_0(t-\epsilon)/2}\left[e^{i\omega(t+\epsilon)/2} - e^{-i\omega(t+\epsilon)/2}\right] = -\frac{i\alpha^*}{\epsilon\hbar\omega}e^{i\omega_0(t-\epsilon)/2}\sin\left[\frac{\omega(t+\epsilon)}{2}\right]. \end{aligned}$$

Thus

$$a = c_a(\epsilon) = e^{-i\omega_0\epsilon}\left[\cos(\omega\epsilon) + i\frac{\omega_0}{\omega}\sin(\omega\epsilon)\right], \quad b = c_b(\epsilon) = -\frac{i\alpha^*}{\epsilon\hbar\omega}\sin(\omega\epsilon).$$

This is for the rectangular pulse; it remains to take the limit $\epsilon \to 0$: $\omega \to |\alpha|/\epsilon\hbar$, so

$$a \to \cos\left(\frac{|\alpha|}{\hbar}\right) + i\frac{\omega_0\epsilon\hbar}{|\alpha|}\sin\left(\frac{|\alpha|}{\hbar}\right) \to \cos\left(\frac{|\alpha|}{\hbar}\right), \quad b \to -\frac{i\alpha^*}{|\alpha|}\sin\left(\frac{|\alpha|}{\hbar}\right),$$

and we conclude that for the delta function

$$\boxed{\begin{aligned} c_a(t) &= \begin{cases} 1, & t<0, \\ \cos(|\alpha|/\hbar), & t>0; \end{cases} \\ c_b(t) &= \begin{cases} 0, & t<0, \\ -i\sqrt{\dfrac{\alpha^*}{\alpha}}\sin(|\alpha|/\hbar), & t>0. \end{cases} \end{aligned}}$$

Obviously, $|c_a(t)|^2 + |c_b(t)|^2 = 1$ in both time periods. Finally,

$$\boxed{P_{a\to b} = |b|^2 = \sin^2(|\alpha|/\hbar).}$$

Problem 9.4

(a)

$$\left.\begin{aligned} \text{Eq. 9.10} &\implies \dot{c}_a = -\frac{i}{\hbar}\left[c_a H'_{aa} + c_b H'_{ab} e^{-i\omega_0 t}\right] \\ \text{Eq. 9.11} &\implies \dot{c}_b = -\frac{i}{\hbar}\left[c_b H'_{bb} + c_a H'_{ba} e^{i\omega_0 t}\right] \end{aligned}\right\} \text{(these are } \textit{exact}\text{, and replace Eq. 9.13).}$$

<u>Initial conditions</u>: $c_a(0) = 1, \quad c_b(0) = 0.$

<u>Zeroth order</u>: $c_a(t) = 1, \quad c_b(t) = 0.$

<u>First order</u>: $\begin{cases} \dot{c}_a = -\dfrac{i}{\hbar}H'_{aa} & \Longrightarrow \\ \dot{c}_b = -\dfrac{i}{\hbar}H'_{ba}e^{i\omega_0 t} & \Longrightarrow \end{cases} \boxed{\begin{aligned} c_a(t) &= 1 - \frac{i}{\hbar}\int_0^t H'_{aa}(t')\,dt' \\ c_b(t) &= -\frac{i}{\hbar}\int_0^t H'_{ba}(t')e^{i\omega_0 t'}\,dt' \end{aligned}}$

$$|c_a|^2 = \left[1 - \frac{i}{\hbar}\int_0^t H'_{aa}(t')\,dt'\right]\left[1 + \frac{i}{\hbar}\int_0^t H'_{aa}(t')\,dt'\right] = 1 + \left[\frac{1}{\hbar}\int_0^t H'_{aa}(t')\,dt'\right]^2 = 1 \text{ (to first order in } H'\text{)}.$$

$$|c_b|^2 = \left[-\frac{i}{\hbar}\int_0^t H'_{ba}(t')e^{i\omega_0 t'}\,dt'\right]\left[\frac{i}{\hbar}\int_0^t H'_{ab}(t')e^{-i\omega_0 t'}\,dt'\right] = 0 \text{ (to first order in } H'\text{)}.$$

So $|c_a|^2 + |c_b|^2 = 1$ (to first order).

(b)

$$\dot{d}_a = e^{\frac{i}{\hbar}\int_0^t H'_{aa}(t')\,dt'}\left(\frac{i}{\hbar}H'_{aa}\right)c_a + e^{\frac{i}{\hbar}\int_0^t H'_{aa}(t')\,dt'}\dot{c}_a. \quad \text{But } \dot{c}_a = -\frac{i}{\hbar}\left[c_a H'_{aa} + c_b H'_{ab}e^{-i\omega_0 t}\right]$$

Two terms cancel, leaving

$$\begin{aligned} \dot{d}_a &= -\frac{i}{\hbar}e^{\frac{i}{\hbar}\int_0^t H'_{aa}(t')\,dt'} c_b H'_{ab} e^{-i\omega_0 t}. \quad \text{But } c_b = e^{-\frac{i}{\hbar}\int_0^t H'_{bb}(t')\,dt'} d_b. \\ &= -\frac{i}{\hbar}e^{\frac{i}{\hbar}\int_0^t [H'_{aa}(t') - H'_{bb}(t')]dt'} H'_{ab}e^{-i\omega_0 t} d_b, \quad \text{or} \quad \dot{d}_a = -\frac{i}{\hbar}e^{i\phi}H'_{ab}e^{-i\omega_0 t}d_b. \end{aligned}$$

Similarly,

$$\begin{aligned}
\dot{d}_b &= e^{\frac{i}{\hbar}\int_0^t H'_{bb}(t')\,dt'}\left(\frac{i}{\hbar}H'_{bb}\right)c_b + e^{\frac{i}{\hbar}\int_0^t H'_{bb}(t')\,dt'}\dot{c}_b. \quad \text{But } \dot{c}_b = -\frac{i}{\hbar}\left[c_b H'_{bb} + c_a H'_{ba}e^{i\omega_0 t}\right].\\
&= -\frac{i}{\hbar}e^{\frac{i}{\hbar}\int_0^t H'_{bb}(t')\,dt'}c_a H'_{ba}e^{i\omega_0 t}. \quad \text{But } c_a = e^{-\frac{i}{\hbar}\int_0^t H'_{aa}(t')\,dt'}d_a.\\
&= -\frac{i}{\hbar}e^{\frac{i}{\hbar}\int_0^t\left[H'_{bb}(t')-H'_{aa}(t')\right]dt'}H'_{ba}e^{i\omega_0 t}d_a = -\frac{i}{\hbar}e^{-i\phi}H'_{ba}e^{i\omega_0 t}d_a. \quad \text{QED}
\end{aligned}$$

(c)

Initial conditions: $c_a(0) = 1 \Longrightarrow d_a(0) = 1; \quad c_b(0) = 0 \Longrightarrow d_b(0) = 0.$

Zeroth order: $d_a(t) = 1, \quad d_b(t) = 0.$

First order: $\dot{d}_a = 0 \Longrightarrow d_a(t) = 1 \Longrightarrow \boxed{c_a(t) = e^{-\frac{i}{\hbar}\int_0^t H'_{aa}(t')\,dt'}.}$

$$\dot{d}_b = -\frac{i}{\hbar}e^{-i\phi}H'_{ba}e^{i\omega_0 t} \Longrightarrow d_b = -\frac{i}{\hbar}\int_0^t e^{-i\phi(t')}H'_{ba}(t')e^{i\omega_0 t'}\,dt' \Longrightarrow$$

$$\boxed{c_b(t) = -\frac{i}{\hbar}e^{-\frac{i}{\hbar}\int_0^t H'_{bb}(t')dt'}\int_0^t e^{-i\phi(t')}H'_{ba}(t')e^{i\omega_0 t'}\,dt'.}$$

These don't *look* much like the results in (a), but remember, we're only working to *first order* in H', so $c_a(t) \approx 1 - \frac{i}{\hbar}\int_0^t H'_{aa}(t')\,dt'$ (to this order), while for c_b, the factor H_{ba} in the integral means it is *already* first order and hence both the exponential factor in front and $e^{-i\phi}$ should be replaced by 1. Then $c_b(t) \approx -\frac{i}{\hbar}\int_0^t H'_{ba}(t')e^{i\omega_0 t'}\,dt'$, and we recover the results in (a).

Problem 9.5

Zeroth order: $c_a^{(0)}(t) = a, \quad c_b^{(0)}(t) = b.$

First order:
$$\begin{cases}
\dot{c}_a = -\frac{i}{\hbar}H'_{ab}e^{-i\omega_0 t}b \Longrightarrow c_a^{(1)}(t) = a - \frac{ib}{\hbar}\int_0^t H'_{ab}(t')e^{-i\omega_0 t'}\,dt'.\\
\dot{c}_b = -\frac{i}{\hbar}H'_{ba}e^{i\omega_0 t}a \Longrightarrow c_b^{(1)}(t) = b - \frac{ia}{\hbar}\int_0^t H'_{ba}(t')e^{i\omega_0 t'}\,dt'.
\end{cases}$$

Second order: $\dot{c}_a = -\frac{i}{\hbar}H'_{ab}e^{-i\omega_0 t}\left[b - \frac{ia}{\hbar}\int_0^t H'_{ba}(t')e^{i\omega_0 t'}\,dt'\right] \Longrightarrow$

$$\boxed{c_a^{(2)}(t) = a - \frac{ib}{\hbar}\int_0^t H'_{ab}(t')e^{-i\omega_0 t'}\,dt' - \frac{a}{\hbar^2}\int_0^t H'_{ab}(t')e^{-i\omega_0 t'}\left[\int_0^{t'} H'_{ba}(t'')e^{i\omega_0 t''}\,dt''\right]dt'.}$$

To get c_b, just switch $a \leftrightarrow b$ (which entails also changing the sign of ω_0):

$$\boxed{c_b^{(2)}(t) = b - \frac{ia}{\hbar}\int_0^t H'_{ba}(t')e^{i\omega_0 t'}\,dt' - \frac{b}{\hbar^2}\int_0^t H'_{ba}(t')e^{i\omega_0 t'}\left[\int_0^{t'} H'_{ab}(t'')e^{-i\omega_0 t''}\,dt''\right]dt'.}$$

Problem 9.6

For H' independent of t, Eq. 9.17 $\Longrightarrow c_b^{(2)}(t) = c_b^{(1)}(t) = -\frac{i}{\hbar}H'_{ba}\int_0^t e^{i\omega_0 t'}dt' \Longrightarrow$

$$c_b^{(2)}(t) = -\frac{i}{\hbar}H'_{ba}\left.\frac{e^{i\omega_0 t'}}{i\omega_0}\right|_0^t = \boxed{-\frac{H'_{ba}}{\hbar\omega_0}\left(e^{i\omega_0 t}-1\right).}\quad \text{Meanwhile Eq. 9.18} \Longrightarrow$$

$$\begin{aligned} c_a^{(2)}(t) &= 1 - \frac{1}{\hbar^2}|H'_{ab}|^2\int_0^t e^{-i\omega_0 t'}\left[\int_0^{t'} e^{i\omega_0 t''}dt''\right]dt' = 1 - \frac{1}{\hbar^2}|H'_{ab}|^2\frac{1}{i\omega_0}\int_0^t\left(1-e^{-i\omega_0 t'}\right)dt' \\ &= 1 + \frac{i}{\omega_0\hbar^2}|H'_{ab}|^2\left.\left(t' + \frac{e^{-i\omega_0 t'}}{i\omega_0}\right)\right|_0^t = \boxed{1 + \frac{i}{\omega_0\hbar^2}|H'_{ab}|^2\left[t + \frac{1}{i\omega_0}\left(e^{-i\omega_0 t}-1\right)\right].} \end{aligned}$$

For comparison with the exact answers (Problem 9.2), note first that $c_b(t)$ is already first order (because of the H'_{ba} in front), whereas ω differs from ω_0 only in second order, so it suffices to replace $\omega \to \omega_0$ in the exact formula to get the second-order result:

$$c_b(t) \approx \frac{2H'_{ba}}{i\hbar\omega_0}e^{i\omega_0 t/2}\sin(\omega_0 t/2) = \frac{2H'_{ba}}{i\hbar\omega_0}e^{i\omega_0 t/2}\frac{1}{2i}\left(e^{i\omega_0 t/2} - e^{-i\omega_0 t/2}\right) = -\frac{H'_{ba}}{\hbar\omega_0}\left(e^{i\omega_0 t}-1\right),$$

in agreement with the result above. Checking c_a is more difficult. Note that

$$\omega = \omega_0\sqrt{1 + \frac{4|H'_{ab}|^2}{\omega_0^2\hbar^2}} \approx \omega_0\left(1 + 2\frac{|H'_{ab}|^2}{\omega_0^2\hbar^2}\right) = \omega_0 + 2\frac{|H'_{ab}|^2}{\omega_0\hbar^2};\quad \frac{\omega_0}{\omega} \approx 1 - 2\frac{|H'_{ab}|^2}{\omega_0^2\hbar^2}.$$

Taylor expansion:

$$\begin{cases} \cos(x+\epsilon) = \cos x - \epsilon\sin x \Longrightarrow \cos(\omega t/2) = \cos\left(\frac{\omega_0 t}{2} + \frac{|H'_{ab}|^2 t}{\omega_0\hbar^2}\right) \approx \cos(\omega_0 t/2) - \frac{|H'_{ab}|^2 t}{\omega_0\hbar^2}\sin(\omega_0 t/2) \\ \sin(x+\epsilon) = \sin x + \epsilon\cos x \Longrightarrow \sin(\omega t/2) = \sin\left(\frac{\omega_0 t}{2} + \frac{|H'_{ab}|^2 t}{\omega_0\hbar^2}\right) \approx \sin(\omega_0 t/2) + \frac{|H'_{ab}|^2 t}{\omega_0\hbar^2}\cos(\omega_0 t/2) \end{cases}$$

$$\begin{aligned} c_a(t) &\approx e^{-i\omega_0 t/2}\left\{\cos\left(\frac{\omega_0 t}{2}\right) - \frac{|H'_{ab}|^2 t}{\omega_0\hbar^2}\sin\left(\frac{\omega_0 t}{2}\right) + i\left(1 - 2\frac{|H'_{ab}|^2}{\omega_0^2\hbar^2}\right)\left[\sin\left(\frac{\omega_0 t}{2}\right) + \frac{|H'_{ab}|^2 t}{\omega_0\hbar^2}\cos\left(\frac{\omega_0 t}{2}\right)\right]\right\} \\ &= e^{-i\omega_0 t/2}\left\{\left[\cos\left(\frac{\omega_0 t}{2}\right) + i\sin\left(\frac{\omega_0 t}{2}\right)\right] - \frac{|H'_{ab}|^2}{\omega_0\hbar^2}\left[t\left(\sin\left(\frac{\omega_0 t}{2}\right) - i\cos\left(\frac{\omega_0 t}{2}\right)\right) + \frac{2i}{\omega_0}\sin\left(\frac{\omega_0 t}{2}\right)\right]\right\} \\ &= e^{-i\omega_0 t/2}\left\{e^{i\omega_0 t/2} - \frac{|H'_{ab}|^2}{\omega_0\hbar^2}\left[-ite^{i\omega_0 t/2} + \frac{2i}{\omega}\frac{1}{2i}\left(e^{i\omega_0 t/2} - e^{-i\omega_0 t/2}\right)\right]\right\} \\ &= 1 - \frac{|H'_{ab}|^2}{\omega_0\hbar^2}\left[-it + \frac{1}{\omega_0}\left(1 - e^{-i\omega_0 t}\right)\right] = 1 + \frac{i}{\omega_0\hbar^2}|H'_{ab}|^2\left[t + \frac{1}{i\omega_0}\left(e^{-i\omega_0 t}-1\right)\right],\ \text{as above.}\ \checkmark \end{aligned}$$

Problem 9.7

(a)

$$\dot{c}_a = -\frac{i}{2\hbar}V_{ab}e^{i\omega t}e^{-i\omega_0 t}c_b;\quad \dot{c}_b = -\frac{i}{2\hbar}V_{ba}e^{-i\omega t}e^{i\omega_0 t}c_a.$$

Differentiate the latter, and substitute in the former:

$$\begin{aligned}\ddot{c}_b &= -i\frac{V_{ba}}{2\hbar}\left[i(\omega_0-\omega)e^{i(\omega_0-\omega)t}c_a + e^{i(\omega_0-\omega)t}\dot{c}_a\right]\\ &= i(\omega_0-\omega)\left[-i\frac{V_{ba}}{2\hbar}e^{i(\omega_0-\omega)t}c_a\right] - i\frac{V_{ba}}{2\hbar}e^{i(\omega_0-\omega)t}\left[-i\frac{V_{ab}}{2\hbar}e^{-i(\omega_0-\omega)t}c_b\right] = i(\omega_0-\omega)\dot{c}_b - \frac{|V_{ab}|^2}{(2\hbar)^2}c_b.\end{aligned}$$

$$\frac{d^2c_b}{dt^2} + i(\omega-\omega_0)\frac{dc_b}{dt} + \frac{|V_{ab}|^2}{4\hbar^2}c_b = 0. \quad \text{Solution is of the form } c_b = e^{\lambda t}: \quad \lambda^2 + i(\omega-\omega_0)\lambda + \frac{|V_{ab}|^2}{4\hbar^2} = 0.$$

$$\lambda = \frac{1}{2}\left[-i(\omega-\omega_0) \pm \sqrt{-(\omega-\omega_0)^2 - \frac{|V_{ab}|^2}{\hbar^2}}\right] = i\left[-\frac{(\omega-\omega_0)}{2} \pm \omega_r\right], \text{ with } \omega_r \text{ defined in Eq. 9.30.}$$

General solution: $c_b(t) = Ae^{i\left[-\frac{(\omega-\omega_0)}{2}+\omega_r\right]t} + Be^{i\left[-\frac{(\omega-\omega_0)}{2}+\omega_r\right]t} = e^{-i(\omega-\omega_0)t/2}\left[Ae^{i\omega_r t} + Be^{-i\omega_r t}\right]$,

or, more conveniently: $c_b(t) = e^{-i(\omega-\omega_0)t/2}\left[C\cos(\omega_r t) + D\sin(\omega_r t)\right]$. But $c_b(0) = 0$, so $C = 0$:

$$\begin{aligned}c_b(t) &= De^{i(\omega_0-\omega)t/2}\sin(\omega_r t). \quad \dot{c}_b = D\left[i\left(\frac{\omega_0-\omega}{2}\right)e^{i(\omega_0-\omega)t/2}\sin(\omega_r t) + \omega_r e^{i(\omega_0-\omega)t/2}\cos(\omega_r t)\right];\\ c_a(t) &= i\frac{2\hbar}{V_{ba}}e^{i(\omega-\omega_0)t}\dot{c}_b = i\frac{2\hbar}{V_{ba}}e^{i(\omega-\omega_0)t/2}D\left[i\left(\frac{\omega_0-\omega}{2}\right)\sin(\omega_r t) + \omega_r\cos(\omega_r t)\right]. \quad \text{But } c_a(0) = 1:\\ 1 &= i\frac{2\hbar}{V_{ba}}D\omega_r, \quad \text{or} \quad D = \frac{-iV_{ba}}{2\hbar\omega_r}.\end{aligned}$$

$$\boxed{c_b(t) = -\frac{i}{2\hbar\omega_r}V_{ba}e^{i(\omega_0-\omega)t/2}\sin(\omega_r t), \quad c_a(t) = e^{i(\omega-\omega_0)t/2}\left[\cos(\omega_r t) + i\left(\frac{\omega_0-\omega}{2\omega_r}\right)\sin(\omega_r t)\right].}$$

(b)

$P_{a\to b}(t) = |c_b(t)|^2 = \boxed{\left(\frac{|V_{ab}|}{2\hbar\omega_r}\right)^2\sin^2(\omega_r t).}$ The largest this gets (when $\sin^2 = 1$) is $\dfrac{|V_{ab}|^2/\hbar^2}{4\omega_r^2}$,

and the denominator, $4\omega_r^2 = (\omega-\omega_0)^2 + |V_{ab}|^2/\hbar^2$, exceeds the numerator, so $P \le 1$ (and 1 only if $\omega = \omega_0$).

$$\begin{aligned}|c_a|^2 + |c_b|^2 &= \cos^2(\omega_r t) + \left(\frac{\omega_0-\omega}{2\omega_r}\right)^2\sin^2(\omega_r t) + \left(\frac{|V_{ab}|}{2\hbar\omega_r}\right)^2\sin^2(\omega_r t)\\ &= \cos^2(\omega_r t) + \frac{(\omega-\omega_0)^2 + (|V_{ab}|/\hbar)^2}{4\omega_r^2}\sin^2(\omega_r t) = \cos^2(\omega_r t) + \sin^2(\omega_r t) = 1. \quad \checkmark\end{aligned}$$

(c) If $\boxed{|V_{ab}|^2 \ll \hbar^2(\omega-\omega_0)^2,}$ then $\omega_r \approx \frac{1}{2}|\omega-\omega_0|$, and $P_{a\to b} \approx \dfrac{|V_{ab}|^2}{\hbar^2}\dfrac{\sin^2\left(\frac{\omega-\omega_0}{2}t\right)}{(\omega-\omega_0)^2}$, confirming Eq. 9.28.

(d) $\omega_r t = \pi \Longrightarrow \boxed{t = \pi/\omega_r.}$

Problem 9.8

Spontaneous emission rate (Eq. 9.56): $A = \dfrac{\omega^3|\wp|^2}{3\pi\epsilon_0\hbar c^3}$. Thermally stimulated emission rate (Eq. 9.47):

$$R = \frac{\pi}{3\epsilon_0\hbar^2}|\wp|^2\rho(\omega), \quad \text{with} \quad \rho(\omega) = \frac{\hbar}{\pi^2c^3}\frac{\omega^3}{(e^{\hbar\omega/k_BT}-1)} \quad \text{(Eq. 9.52).}$$

So the ratio is

$$\frac{A}{R} = \frac{\omega^3|\wp|^2}{3\pi\epsilon_0\hbar c^3}\cdot\frac{3\epsilon_0\hbar^2}{\pi|\wp|^2}\cdot\frac{\pi^2c^3\left(e^{\hbar\omega/k_BT}-1\right)}{\hbar\omega^3} = e^{\hbar\omega/k_BT}-1.$$

The ratio is a monotonically increasing function of ω, and is 1 when

$$e^{\hbar\omega/k_bt} = 2, \quad \text{or} \quad \frac{\hbar\omega}{k_BT} = \ln 2, \quad \omega = \frac{k_BT}{\hbar}\ln 2, \quad \text{or} \quad \nu = \frac{\omega}{2\pi} = \frac{k_BT}{h}\ln 2. \quad \text{For } T = 300\text{ K},$$

$$\nu = \frac{(1.38\times 10^{-23}\text{ J/K})(300\text{ K})}{(6.63\times 10^{-34}\text{ J}\cdot\text{s})}\ln 2 = 4.35\times 10^{12}\text{ Hz}.$$

For higher frequencies, (including light, at 10^{14} Hz), spontaneous emission dominates.

Problem 9.9

(a) Simply remove the factor $\left(e^{\hbar\omega/k_BT}-1\right)$ in the denominator of Eq. 5.113: $\boxed{\rho_0(\omega) = \dfrac{\hbar\omega^3}{\pi^2c^3}.}$

(b) Plug this into Eq. 9.47:

$$R_{b\to a} = \frac{\pi}{3\epsilon_0\hbar^2}|\wp|^2\frac{\hbar\omega^3}{\pi^2c^3} = \boxed{\frac{\omega^3|\wp|^2}{3\pi\epsilon_0\hbar c^3},}$$

reproducing Eq. 9.56.

Problem 9.10

$N(t) = e^{-t/\tau}N(0)$ (Eqs. 9.58 and 9.59). After one half-life, $N(t) = \frac{1}{2}N(0)$, so $\frac{1}{2} = e^{-t/\tau}$, or $2 = e^{t/\tau}$, so $t/\tau = \ln 2$, or $\boxed{t_{1/2} = \tau\ln 2.}$

Problem 9.11

In Problem 9.1 we calculated the matrix elements of z; all of them are zero except $\langle 1\,0\,0|z|2\,1\,0\rangle = \dfrac{2^8}{3^5\sqrt{2}}\,a$. As for x and y, we noted that $|1\,0\,0\rangle$, $|2\,0\,0\rangle$, and $|2\,1\,0\rangle$ are *even* (in x, y), whereas $|2\,1\,\pm1\rangle$ is odd. So the only non-zero matrix elements are $\langle 1\,0\,0|x|2\,1\pm1\rangle$ and $\langle 1\,0\,0|y|2\,1\pm1\rangle$. Using the wave functions in Problem 9.1:

$$\begin{aligned}\langle 1\,0\,0|x|2\,1\pm1\rangle &= \frac{1}{\sqrt{\pi a^3}}\left(\frac{\mp1}{8\sqrt{\pi a^3}}\right)\frac{1}{a}\int e^{-r/a}re^{-r/2a}\sin\theta\, e^{\pm i\phi}(r\sin\theta\cos\phi)r^2\sin\theta\,dr\,d\theta\,d\phi\\ &= \mp\frac{1}{8\pi a^4}\int_0^\infty r^4e^{-3r/2a}dr\int_0^\pi\sin^3\theta\,d\theta\int_0^{2\pi}(\cos\phi\pm i\sin\phi)\cos\phi\,d\phi\\ &= \frac{\mp1}{8\pi a^4}\left[4!\left(\frac{2a}{3}\right)^5\right]\left(\frac{4}{3}\right)(\pi)=\mp\frac{2^7}{3^5}a.\end{aligned}$$

$$\begin{aligned}\langle 1\,0\,0|y|2\,1\pm1\rangle &= \frac{\mp1}{8\pi a^4}\left[4!\left[\frac{2a}{3}\right)^5\right]\left(\frac{4}{3}\right)\int_0^{2\pi}(\cos\phi\pm i\sin\phi)\sin\phi\,d\phi\\ &= \frac{\mp1}{8\pi a^4}\left[4!\left(\frac{2a}{3}\right)^5\right]\left(\frac{4}{3}\right)(\pm i\pi)=-i\frac{2^7}{3^5}a.\end{aligned}$$

$$\langle 1\,0\,0|\mathbf{r}|2\,0\,0\rangle=0;\quad \langle 1\,0\,0|\mathbf{r}|2\,1\,0\rangle=\frac{2^7\sqrt{2}}{3^5}a\,\hat{k};\quad \langle 1\,0\,0|\mathbf{r}|2\,1\pm1\rangle=\frac{2^7}{3^5}a\left(\mp\hat{\imath}-i\,\hat{\jmath}\right),\ \text{and hence}$$

$$\wp^2=0\ (\text{for } |2\,0\,0\rangle\to|1\,0\,0\rangle),\quad \text{and } |\wp|^2=(qa)^2\frac{2^{15}}{3^{10}}\ (\text{for } |2\,1\,0\rangle\to 1\,0\,0\rangle \text{ and } |2\,1\pm1\rangle\to|1\,0\,0\rangle).$$

Meanwhile, $\omega=\dfrac{E_2-E_1}{\hbar}=\dfrac{1}{\hbar}\left(\dfrac{E_1}{4}-E_1\right)=-\dfrac{3E_1}{4\hbar}$, so for the three $l=1$ states:

$$\begin{aligned}A &= -\frac{3^3E_1^3}{2^6\hbar^3}\frac{(ea)^2 2^{15}}{3^{10}}\frac{1}{3\pi\epsilon_0\hbar c^3}=-\frac{2^9}{3^8\pi}\frac{E_1^3e^2a^2}{\epsilon_0\hbar^4c^3}=\frac{2^{10}}{3^8}\left(\frac{E_1}{mc^2}\right)^2\frac{c}{a}\\ &= \frac{2^{10}}{3^8}\left(\frac{13.6}{0.511\times10^6}\right)^2\frac{(3.00\times10^8\text{ m/s})}{(0.529\times10^{-10}\text{ m})}=6.27\times10^8/\text{s};\quad \tau=\frac{1}{A}=\boxed{1.60\times10^{-9}\text{ s}}\end{aligned}$$

for the three $l=1$ states (all have the *same* lifetime); $\boxed{\tau=\infty}$ for the $l=0$ state.

Problem 9.12

$$[L^2,z]=[L_x^2,z]+[L_y^2,z]+[L_z^2,z]=L_x[L_x,z]+[L_x,z]L_x+L_y[L_y,z]+[L_y,z]L_y+L_z[L_z,z]+[L_z,z]L_z$$

$$\text{But}\ \begin{cases}[L_x,z]=[yp_z-zp_y,z]=[yp_z,z]-[zp_y,z]=y[p_z,z]=-i\hbar y,\\ [L_y,z]=[zp_x-xp_z,z]=[zp_x,z]-[xp_z,z]=-x[p_z,z]=i\hbar x,\\ [L_z,z]=[xp_y-yp_x,z]=[xp_y,z]-[yp_x,z]=0.\end{cases}$$

So: $\quad [L^2,z]=L_x(-i\hbar y)+(-i\hbar y)L_x+L_y(i\hbar x)+(i\hbar x)L_y=i\hbar(-L_xy-yL_x+L_yx+xL_y).$

$$\text{But}\ \begin{cases}L_xy=L_xy-yL_x+yL_x=[L_x,y]+yL_x=i\hbar z+yL_x,\\ L_yx=L_yx-xL_y+xL_y=[L_y,x]+xL_y=-i\hbar z+xL_y.\end{cases}$$

So: $[L^2, z] = i\hbar(2xL_y - i\hbar z - 2yL_x - i\hbar z) \Longrightarrow \boxed{[L^2, z] = 2i\hbar(xL_y - yL_x - i\hbar z).}$

$$\begin{aligned}\left[L^2,[L^2,z]\right] &= 2i\hbar\left\{[L^2, xL_y] - [L^2, yL_x] - i\hbar[L^2,z]\right\}\\ &= 2i\hbar\left\{[L^2,x]L_y + x[L^2,L_y] - [L^2,y]L_x - y[L^2,L_x] - i\hbar(L^2z - zL^2)\right\}.\end{aligned}$$

But $[L^2, L_y] = [L^2, L_x] = 0$ (Eq. 4.102), so

$$\left[L^2,[L^2,z]\right] = 2i\hbar\left\{(yL_z - zL_y - i\hbar x)\,L_y - 2i\hbar\,(zL_x - xL_z - i\hbar y)\,L_x - i\hbar\left(L^2z - zL^2\right)\right\},\ \text{or}$$

$$\begin{aligned}\left[L^2,[L^2,z]\right] &= -2\hbar^2\Bigg(2yL_zL_y \quad \underbrace{-2zL_y^2 - 2zL_x^2}_{-2z(L_x^2+L_y^2+L_z^2)+2zL_z^2} \quad -2i\hbar xL_y + 2xL_zL_x + 2i\hbar yL_x - L^2z + zL^2\Bigg)\\ &= -2\hbar^2\left(2yL_zL_y - 2i\hbar xL_y + 2xL_zL_x + 2i\hbar yL_x + 2zL_z^2 - 2zL^2 - L^2z + zL^2\right)\\ &= -2\hbar^2\left(zL^2 + L^2z\right) - 4\hbar^2\Bigg[\underbrace{(yL_z - i\hbar x)}_{L_zy}L_y + \underbrace{(xL_z + i\hbar y)}_{L_zx}L_x + zL_zL_z\Bigg]\\ &= 2\hbar^2\left(zL^2 + L^2z\right) - 4\hbar^2\underbrace{\left(L_zyL_y + L_zxL_x + L_zzL_z\right)}_{L_z(\mathbf{r}\cdot\mathbf{L})=0} = 2\hbar^2(zL^2 + L^2z). \quad \text{QED}\end{aligned}$$

Problem 9.13

$$|n\,0\,0\rangle = R_{n0}(r)Y_0^0(\theta,\phi) = \frac{1}{\sqrt{4\pi}}R_{n0}(r), \quad \text{so} \quad \langle n'\,0\,0|\mathbf{r}|n\,0\,0\rangle = \frac{1}{4\pi}\int R_{n'0}(r)R_{n0}(r)(x\,\hat{\imath} + y\,\hat{\jmath} + z\,\hat{k})\,dx\,dy\,dz.$$

But the integrand is odd in x, y, or z, so the integral is zero.

Problem 9.14

(a)

$$\boxed{|3\,0\,0\rangle \rightarrow \left\{\begin{array}{c}|2\,1\,0\rangle\\ |2\,1\,1\rangle\\ |2\,1{-}1\rangle\end{array}\right\} \rightarrow |1\,0\,0\rangle.} \quad (|3\,0\,0\rangle \rightarrow |2\,0\,0\rangle \text{ and } |3\ 0\ 0\rangle \rightarrow |1\ 0\ 0\rangle \text{ violate } \Delta l = \pm 1 \text{ rule.})$$

(b)

From Eq. 9.72: $\langle 2\,1\,0|\mathbf{r}|3\,0\,0\rangle = \langle 2\,1\,0|z|3\,0\,0\rangle\,\hat{k}$.

From Eq. 9.69: $\langle 2\,1\pm1|\mathbf{r}|3\,0\,0\rangle = \langle 2\,1\pm1|x|3\,0\,0\rangle\,\hat{\imath} + \langle 2\,1\pm1|y|3\,0\,0\rangle\,\hat{\jmath}$.

From Eq. 9.70: $\pm\langle 2\,1\pm1|x|3\,0\,0\rangle = i\langle 2\,1\pm1|y|3\,0\,0\rangle$.

Thus $|\langle 2\,1\,0|\mathbf{r}|3\,0\,0\rangle|^2 = |\langle 2\,1\,0|z|3\,0\,0\rangle|^2$ and $|\langle 2\,1\pm1|\mathbf{r}|3\,0\,0\rangle|^2 = 2|\langle 2\,1\pm1|x|3\,0\,0\rangle|^2$, so there are really just two matrix elements to calculate.

$\psi_{21m} = R_{21}Y_1^m, \quad \psi_{300} = R_{30}Y_0^0.$ From Table 4.3:

$$\int Y_1^0 Y_0^0 \cos\theta \sin\theta \, d\theta \, d\phi = \sqrt{\frac{3}{4\pi}}\sqrt{\frac{1}{4\pi}} \int_0^\pi \cos^2\theta \sin\theta \, d\theta \int_0^{2\pi} d\phi = \frac{\sqrt{3}}{4\pi}\left(-\frac{\cos^3\theta}{3}\right)\Bigg|_0^\pi (2\pi) = \frac{\sqrt{3}}{2}\left(\frac{2}{3}\right) = \frac{1}{\sqrt{3}}.$$

$$\int \left(Y_1^{\pm1}\right)^* Y_0^0 \sin^2\theta \cos\phi \, d\theta \, d\phi = \mp\sqrt{\frac{3}{8\pi}}\sqrt{\frac{1}{4\pi}} \int_0^\pi \sin^3\theta \, d\theta \int_0^{2\pi} \cos\phi e^{\mp i\phi} \, d\phi$$

$$= \mp\frac{1}{4\pi}\sqrt{\frac{3}{2}}\left(\frac{4}{3}\right)\left[\int_0^{2\pi} \cos^2\phi \, d\phi \mp i \int_0^{2\pi} \cos\phi \sin\phi \, d\phi\right] = \mp\frac{1}{\pi\sqrt{6}}(\pi \mp 0) = \mp\frac{1}{\sqrt{6}}.$$

From Table 4.7:

$$K \equiv \int_0^\infty R_{21}R_{30}\, r^3 \, dr = \frac{1}{\sqrt{24}a^{3/2}}\frac{2}{\sqrt{27}a^{3/2}} \int_0^\infty \frac{r}{a}e^{-r/2a}\left[1 - \frac{2}{3}\frac{r}{a} + \frac{2}{27}\left(\frac{r}{a}\right)^2\right] e^{-r/3a} r^3 \, dr$$
$$= \frac{1}{9\sqrt{2}a^3}a^4 \int_0^\infty \left(1 - \frac{2}{3}u + \frac{2}{27}u^2\right) u^4 e^{-5u/6} \, du = \frac{a}{9\sqrt{2}}\left[4!\left(\frac{6}{5}\right)^5 - \frac{2}{3}5!\left(\frac{6}{5}\right)^6 + \frac{2}{27}6!\left(\frac{6}{5}\right)^7\right]$$
$$= \frac{a}{9\sqrt{2}}\frac{4!\,6^5}{5^6}\left(5 - \frac{2}{3}6\cdot 5 + \frac{2}{27}6^3\right) = \frac{a}{9\sqrt{2}}\frac{4!\,6^5}{5^6} = \frac{2^7 3^4}{5^6}\sqrt{2}\,a.$$

So:

$$\langle 2\,1 \pm 1|x|3\,0\,0\rangle = \int R_{21}(Y_1^{\pm1})^*(r\sin\theta\cos\phi)R_{30}Y_0^0\, r^2 \sin\theta \, dr \, d\theta \, d\phi = K\left(\mp\frac{1}{\sqrt{6}}\right).$$
$$\langle 2\,1\,0|z|3\,0\,0\rangle = \int R_{21}Y_1^0(r\cos\theta)R_{30}Y_0^0\, r^2 \sin\theta \, dr \, d\theta \, d\phi = K\left(\frac{1}{\sqrt{3}}\right).$$

$$|\langle 2\,1\,0|\mathbf{r}|3\,0\,0\rangle|^2 = |\langle 2\,1\,0|z|3\,0\,0\rangle|^2 = K^2/3;$$

$$|\langle 2\,1 \pm 1|\mathbf{r}|3\,0\,0\,\rangle|^2 = 2|\langle 2\,1 \pm 1|x|3\,0\,0\,\rangle|^2 = K^2/3.$$

Evidently the three transition rates are *equal*, and hence $\boxed{1/3}$ go by each route.

(c) For each mode, $A = \dfrac{\omega^3 e^2 |\langle\mathbf{r}\rangle|^2}{3\pi\epsilon_0\hbar c^3}$; here $\omega = \dfrac{E_3 - E_2}{\hbar} = \dfrac{1}{\hbar}\left(\dfrac{E_1}{9} - \dfrac{E_1}{4}\right) = -\dfrac{5}{36}\dfrac{E_1}{\hbar}$, so the *total* decay rate is

$$R = 3\left(-\frac{5}{36}\frac{E_1}{\hbar}\right)^3 \frac{e^2}{3\pi\epsilon_0\hbar c^3}\frac{1}{3}\left(\frac{2^7 3^4}{5^6}\sqrt{2}a\right)^2 = 6\left(\frac{2}{5}\right)^9\left(\frac{E_1}{mc^2}\right)^2\left(\frac{c}{a}\right)$$
$$= 6\left(\frac{2}{5}\right)^9\left(\frac{13.6}{0.511\times 10^6}\right)^2\left(\frac{3\times 10^8}{0.529\times 10^{-10}}\right)/\text{s} = 6.32\times 10^6/\text{s}. \quad \tau = \frac{1}{R} = \boxed{1.58\times 10^{-7}\text{ s.}}$$

Problem 9.15

(a)

$$\Psi(t) = \sum c_n(t) e^{-iE_n t/\hbar}\psi_n. \quad H\Psi = i\hbar\frac{\partial \Psi}{\partial t}; \quad H = H_0 + H'(t); \quad H_0\psi_n = E_n\psi_n. \quad \text{So}$$

$$\sum c_n e^{-iE_n t/\hbar} E_n\psi_n + \sum c_n e^{-iE_n t/\hbar} H'\psi_n = i\hbar \sum \dot{c}_n e^{-iE_n t/\hbar}\psi_n + i\hbar\left(-\frac{i}{\hbar}\right)\sum c_n E_n e^{-iE_n t/\hbar}\psi_n.$$

The first and last terms cancel, so

$$\sum c_n e^{-iE_n t/\hbar} H'\psi_n = i\hbar \sum \dot{c}_n e^{-iE_n t/\hbar}\psi_n. \quad \text{Take the inner product with } \psi_m:$$

$$\sum c_n e^{-iE_n t/\hbar}\langle\psi_m|H'|\psi_n\rangle = i\hbar\sum \dot{c}_n e^{-iE_n t/\hbar}\langle\psi_m|\psi_n\rangle.$$

Assume orthonormality of the unperturbed states, $\langle\psi_m|\psi_n\rangle = \delta_{mn}$, and define $H'_{mn} \equiv \langle\psi_m|H'|\psi_n\rangle$.

$$\sum c_n e^{-iE_n t/\hbar} H'_{mn} = i\hbar\,\dot{c}_m e^{-iE_m t/\hbar}, \quad \text{or} \quad \boxed{\dot{c}_m = -\frac{i}{\hbar}\sum_n c_n H'_{mn} e^{i(E_m-E_n)t/\hbar}.}$$

(b) Zeroth order: $c_N(t) = 1$, $c_m(t) = 0$ for $m \neq N$. Then in first order:

$$\dot{c}_N = -\frac{i}{\hbar}H'_{NN}, \quad \text{or} \quad \boxed{c_N(t) = 1 - \frac{i}{\hbar}\int_0^t H'_{NN}(t')\,dt',} \text{ whereas for } m \neq N:$$

$$\dot{c}_m = -\frac{i}{\hbar}H'_{mN}e^{i(E_m-E_N)t/\hbar}, \quad \text{or} \quad \boxed{c_m(t) = -\frac{i}{\hbar}\int_0^t H'_{mN}(t')e^{i(E_m-E_N)t'/\hbar}\,dt'.}$$

(c)

$$\begin{aligned} c_M(t) &= -\frac{i}{\hbar}H'_{MN}\int_0^t e^{i(E_M-E_N)t'/\hbar}\,dt' = -\frac{i}{\hbar}H'_{MN}\left[\frac{e^{i(E_M-E_N)t'/\hbar}}{i(E_M-E_N)/\hbar}\right]\Bigg|_0^t = -H'_{MN}\left[\frac{e^{i(E_M-E_N)t/\hbar}-1}{E_M-E_N}\right] \\ &= -\frac{H'_{MN}}{(E_M-E_N)}e^{i(E_M-E_N)t/2\hbar}\,2i\sin\left(\frac{E_M-E_N}{2\hbar}t\right). \end{aligned}$$

$$P_{N\to M} = |c_M|^2 = \boxed{\frac{4|H'_{MN}|^2}{(E_M-E_N)^2}\sin^2\left(\frac{E_M-E_N}{2\hbar}t\right).}$$

(d)

$$\begin{aligned} c_M(t) &= -\frac{i}{\hbar}V_{MN}\frac{1}{2}\int_0^t\left(e^{i\omega t'} + e^{-i\omega t'}\right)e^{i(E_M-E_N)t'/\hbar}\,dt' \\ &= -\frac{iV_{MN}}{2\hbar}\left[\frac{e^{i(\hbar\omega+E_M-E_N)t'/\hbar}}{i(\hbar\omega+E_M-E_N)/\hbar} + \frac{e^{i(-\hbar\omega+E_M-E_N)t'/\hbar}}{i(-\hbar\omega+E_M-E_N)/\hbar}\right]\Bigg|_0^t. \end{aligned}$$

If $E_M > E_N$, the second term dominates, and transitions occur only for $\omega \approx (E_M - E_N)/\hbar$:

$$c_M(t) \approx -\frac{iV_{MN}}{2\hbar}\frac{1}{(i/\hbar)(E_M - E_N - \hbar\omega)}e^{i(E_M-E_N-\hbar\omega)t/2\hbar}\,2i\sin\left(\frac{E_M - E_N - \hbar\omega}{2\hbar}t\right), \text{ so}$$

$$P_{N\to M} = |c_M|^2 = \frac{|V_{MN}|^2}{(E_M - E_N - \hbar\omega)^2}\sin^2\left(\frac{E_M - E_N - \hbar\omega}{2\hbar}t\right).$$

If $E_M < E_N$ the first term dominates, and transitions occur only for $\omega \approx (E_N - E_M)/\hbar$:

$$c_M(t) \approx -\frac{iV_{MN}}{2\hbar}\frac{1}{(i/\hbar)(E_M - E_N + \hbar\omega)}\,e^{i(E_M-E_N+\hbar\omega)t/2\hbar}\,2i\sin\left(\frac{E_M - E_N + \hbar\omega}{2\hbar}t\right), \text{ and hence}$$

$$P_{N\to M} = \frac{|V_{MN}|^2}{(E_M - E_N + \hbar\omega)^2}\sin^2\left(\frac{E_M - E_N + \hbar\omega}{2\hbar}t\right).$$

Combining the two results, we conclude that transitions occur to states with energy $E_M \approx E_N \pm \hbar\omega$, and

$$\boxed{P_{N\to M} = \frac{|V_{MN}|^2}{(E_M - E_N \pm \hbar\omega)^2}\sin^2\left(\frac{E_M - E_N \pm \hbar\omega}{2\hbar}t\right).}$$

(e) For light, $V_{ba} = -\wp E_0$ (Eq. 9.34). The rest is as before (Section 9.2.3), leading to Eq. 9.47:

$$\boxed{R_{N\to M} = \frac{\pi}{3\epsilon_0\hbar^2}|\wp|^2\rho(\omega), \text{ with } \omega = \pm(E_M - E_N)/\hbar} \quad (+\text{ sign} \Rightarrow \text{absorption}, -\text{ sign} \Rightarrow \text{stimulated emission}).$$

Problem 9.16

For example (c):

$$\boxed{c_N(t) = 1 - \frac{i}{\hbar}H'_{NN}t; \quad c_m(t) = -2i\frac{H'_{mN}}{(E_m - E_N)}e^{i(E_m-E_N)t/2\hbar}\sin\left(\frac{E_m - E_N}{2\hbar}t\right) \;\; (m \neq N).}$$

$$|c_N|^2 = 1 + \frac{1}{\hbar^2}|H'_{NN}|^2t^2, \quad |c_m|^2 = 4\frac{|H'_{mN}|^2}{(E_m - E_N)^2}\sin^2\left(\frac{E_m - E_N}{2\hbar}t\right), \text{ so}$$

$$\sum_m |c_m|^2 = 1 + \frac{t^2}{\hbar^2}|H'_{NN}|^2 + 4\sum_{m\neq N}\frac{|H'_{mN}|^2}{(E_m - E_N)^2}\sin^2\left(\frac{E_m - E_N}{2\hbar}t\right).$$

This is plainly *greater* than 1! But remember: The c's are accurate only to *first* order in H'; to this order the $|H'|^2$ terms do not belong. Only if terms of *first* order appeared in the sum would there be a genuine problem with normalization.

For example (d):

$$c_N = 1 - \frac{i}{\hbar}V_{NN}\int_0^t \cos(\omega t')\,dt' = 1 - \frac{i}{\hbar}V_{NN}\left.\frac{\sin(\omega t')}{\omega}\right|_0^t \Longrightarrow \boxed{c_N(t) = 1 - \frac{i}{\hbar\omega}V_{NN}\sin(\omega t).}$$

$$\boxed{c_m(t) = -\frac{V_{mN}}{2}\left[\frac{e^{i(E_m-E_N+\hbar\omega)t/\hbar}-1}{(E_m-E_N+\hbar\omega)} + \frac{e^{i(E_m-E_N-\hbar\omega)t/\hbar}-1}{(E_m-E_N-\hbar\omega)}\right]\ (m \neq N).}$$ So

$$|c_N|^2 = 1 + \frac{|V_{NN}|^2}{(\hbar\omega)^2}\sin^2(\omega t);\quad \text{and in the rotating wave approximation}$$

$$|c_m|^2 = \frac{|V_{mN}|^2}{(E_m-E_N\pm\hbar\omega)^2}\sin^2\left(\frac{E_m-E_N\pm\hbar\omega}{2\hbar}t\right)\quad (m\neq N).$$

Again, ostensibly $\sum|c_m|^2 > 1$, but the "extra" terms are of *second* order in H', and hence do not belong (to first order).

You would do $\boxed{\text{better to use } 1-\sum_{m\neq N}|c_m|^2.}$ Schematically: $c_m = a_1H + a_2H^2 + \cdots$, so $|c_m|^2 = a_1^2H^2 + 2a_1a_2H^3 + \cdots$, whereas $c_N = 1 + b_1H + b_2H^2 + \cdots$, so $|c_N|^2 = 1 + 2b_1H + (2b_2 + b_1^2)H^2 + \cdots$. Thus knowing c_m to *first* order (i.e., knowing a_1) gets you $|c_m|^2$ to *second* order, but knowing c_N to first order (i.e., b_1) does *not* get you $|c_N|^2$ to second order (you'd also need b_2). It is precisely this b_2 term that would cancel the "extra" (second-order) terms in the calculations of $\sum|c_m|^2$ above.

Problem 9.17

(a)

$$\text{Equation 9.82} \Rightarrow \dot{c}_m = -\frac{i}{\hbar}\sum_n c_n H'_{mn}e^{i(E_m-E_n)t/\hbar}.\quad \text{Here } H'_{mn} = \langle\psi_m|V_0(t)|\psi_n\rangle = \delta_{mn}V_0(t).$$

$$\dot{c}_m = -\frac{i}{\hbar}c_mV_0(t);\quad \frac{dc_m}{c_m} = -\frac{i}{\hbar}V_0(t)\,dt \Rightarrow \ln c_m = -\frac{i}{\hbar}\int V_0(t')\,dt' + constant.$$

$$c_m(t) = c_m(0)e^{-\frac{i}{\hbar}\int_0^t V_0(t')\,dt'}.\quad \text{Let } \Phi(t) \equiv -\frac{1}{\hbar}\int_0^t V_0(t')\,dt';\quad c_m(t) = e^{i\Phi}c_m(0).\quad \text{Hence}$$

$$|c_m(t)|^2 = |c_m(0)|^2, \text{ and there are } no \text{ transitions.}\qquad \boxed{\Phi(T) = -\frac{1}{\hbar}\int_0^T V_0(t)\,dt.}$$

(b)

$$\left.\begin{array}{l} \text{Eq. 9.84} \Rightarrow c_N(t) \approx 1 - \frac{i}{\hbar}\int_0^t V_0(t')\,dt = 1 + i\Phi. \\ \text{Eq. 9.85} \Rightarrow c_m(t) = -\frac{i}{\hbar}\int_0^t \delta_{mN}V_0(t')e^{i(E_m-E_N)t'/\hbar}\,dt' = 0\ (m\neq N). \end{array}\right\}\ \boxed{\begin{array}{l} c_N(t) = 1 + i\Phi(t), \\ c_m(t) = 0\ (m\neq N). \end{array}}$$

The *exact* answer is $c_N(t) = e^{i\Phi(t)}$, $c_m(t) = 0$, and they *are* consistent, since $e^{i\Phi} \approx 1 + i\Phi$, to first order.

Problem 9.18

Use result of Problem 9.15(c). Here $E_n = \dfrac{n^2\pi^2\hbar^2}{2ma^2}$, so $E_2 - E_1 = \dfrac{3\pi^2\hbar^2}{2ma^2}$.

$$\begin{aligned} H'_{12} &= \frac{2}{a}\int_0^{a/2} \sin\left(\frac{\pi}{a}x\right) V_0 \sin\left(\frac{2\pi}{a}x\right) dx \\ &= \frac{2V_0}{a}\left[\frac{\sin\left(\frac{\pi}{a}x\right)}{2(\pi/a)} - \frac{\sin\left(\frac{3\pi}{a}x\right)}{2(3\pi/a)}\right]\Bigg|_0^{a/2} = \frac{V_0}{\pi}\left[\sin\left(\frac{\pi}{2}\right) - \frac{1}{3}\sin\left(\frac{3\pi}{2}\right)\right] = \frac{4V_0}{3\pi}. \end{aligned}$$

$$\text{Eq. 9.86} \implies P_{1\to 2} = 4\left(\frac{4V_0}{3\pi}\right)\left(\frac{2ma^2}{3\pi^2\hbar^2}\right)^2 \sin^2\left(\frac{3\pi^2\hbar}{4ma^2}t\right) = \boxed{\left[\frac{16ma^2V_0}{9\pi^3\hbar^2}\sin\left(\frac{3\pi^2\hbar T}{4ma^2}\right)\right]^2.}$$

[Actually, in this case H'_{11} and H'_{22} are nonzero:

$$H'_{11} = \langle\psi_1|H'|\psi_1\rangle = \frac{2}{a}V_0\int_0^{a/2}\sin^2\left(\frac{\pi}{a}x\right)dx = \frac{V_0}{2}, \quad H'_{22} = \langle\psi_2|H'|\psi_2\rangle = \frac{2}{a}V_0\int_0^{a/2}\sin^2\left(\frac{2\pi}{a}x\right)dx = \frac{V_0}{2}.$$

However, this does not affect the answer, for according to Problem 9.4, $c_1(t)$ picks up an innocuous phase factor, while $c_2(t)$ is not affected at all, in first order (formally, this is because H'_{bb} is multiplied by c_b, in Eq. 9.11, and in zeroth order $c_b(t) = 0$).]

Problem 9.19

Spontaneous absorption would involve taking energy (a photon) from the ground state of the electromagnetic field. But you can't *do* that, because the gound state already has the lowest allowed energy.

Problem 9.20

(a)

$$\begin{aligned} H &= -\gamma\mathbf{B}\cdot\mathbf{S} = -\gamma\left(B_xS_x + B_yS_y + B_zS_z\right); \\ \mathsf{H} &= -\gamma\frac{\hbar}{2}\left(B_x\sigma_x + B_y\sigma_y + B_z\sigma_z\right) = -\frac{\gamma\hbar}{2}\left[B_x\begin{pmatrix}0 & 1\\ 1 & 0\end{pmatrix} + B_y\begin{pmatrix}0 & -i\\ i & 0\end{pmatrix} + B_z\begin{pmatrix}1 & 0\\ 0 & -1\end{pmatrix}\right] \\ &= -\frac{\gamma\hbar}{2}\begin{pmatrix}B_z & B_x - iB_y\\ B_x + iB_y & -B_z\end{pmatrix} = -\frac{\gamma\hbar}{2}\begin{pmatrix}B_0 & B_{\text{rf}}(\cos\omega t + i\sin\omega t)\\ B_{\text{rf}}(\cos\omega t - i\sin\omega t) & -B_0\end{pmatrix} \\ &= \boxed{-\frac{\gamma\hbar}{2}\begin{pmatrix}B_0 & B_{\text{rf}}e^{i\omega t}\\ B_{\text{rf}}e^{-i\omega t} & -B_0\end{pmatrix}.} \end{aligned}$$

(b) $i\hbar\dot{\chi} = \mathsf{H}\chi \Rightarrow$

$$i\hbar\begin{pmatrix}\dot{a}\\ \dot{b}\end{pmatrix} = -\frac{\gamma\hbar}{2}\begin{pmatrix}B_0 & B_{\text{rf}}e^{i\omega t}\\ B_{\text{rf}}e^{-i\omega t} & -B_0\end{pmatrix}\begin{pmatrix}a\\ b\end{pmatrix} = -\frac{\gamma\hbar}{2}\begin{pmatrix}B_0a & B_{\text{rf}}e^{i\omega t}b\\ B_{\text{rf}}e^{-i\omega t}a & -B_0b\end{pmatrix} \quad \Rightarrow$$

$$\begin{cases} \dot{a} = i\dfrac{\gamma}{2}\left(B_0a + B_{\text{rf}}e^{i\omega t}b\right) = \dfrac{i}{2}\left(\Omega e^{i\omega t}b + \omega_0 a\right), \\ \dot{b} = -i\dfrac{\gamma}{2}\left(B_0b - B_{\text{rf}}e^{-i\omega t}a\right) = \dfrac{i}{2}\left(\Omega e^{-i\omega t}a - \omega_0 b\right). \end{cases}$$

(c) You can decouple the equations by differentiating with respect to t, but it is simpler just to *check* the quoted results. First of all, they clearly satisfy the initial conditions: $a(0) = a_0$ and $b(0) = b_0$. Differentiating a:

$$\begin{aligned}\dot{a} &= \frac{i\omega}{2}a + \left\{-a_0\frac{\omega'}{2}\sin(\omega' t/2) + \frac{i}{\omega'}\left[a_0(\omega_0 - \omega) + b_0\Omega\right]\frac{\omega'}{2}\cos(\omega' t/2)\right\}e^{i\omega t/2} \\ &= \frac{i}{2}e^{i\omega t/2}\left\{\omega a_0\cos(\omega' t/2) + i\frac{\omega}{\omega'}\left[a_0(\omega_0 - \omega) + b_0\Omega\right]\sin(\omega' t/2)\right. \\ &\qquad \left. + i\omega' a_0\sin(\omega' t/2) + \left[a_0(\omega_0 - \omega) + b_0\Omega\right]\cos(\omega' t/2)\right\}\end{aligned}$$

Equation 9.90 says this should be equal to

$$\begin{aligned}\frac{i}{2}\left(\Omega e^{i\omega t}b + \omega_0 a\right) &= \frac{i}{2}e^{i\omega t/2}\left\{\Omega b_0\cos(\omega' t/2) + i\frac{\Omega}{\omega'}\left[b_0(\omega - \omega_0) + a_0\Omega\right]\sin(\omega' t/2)\right. \\ &\qquad \left. + \omega_0 a_0\cos(\omega' t/2) + i\frac{\omega_0}{\omega'}\left[a_0(\omega_0 - \omega) + b_0\Omega\right]\sin(\omega' t/2)\right\}.\end{aligned}$$

By inspection the $\cos(\omega' t/2)$ terms in the two expressions are equal; it remains to check that

$$i\frac{\omega}{\omega'}\left[a_0(\omega_0 - \omega) + b_0\Omega\right] + i\omega' a_0 = i\frac{\Omega}{\omega'}\left[b_0(\omega - \omega_0) + a_0\Omega\right] + i\frac{\omega_0}{\omega'}\left[a_0(\omega_0 - \omega) + b_0\Omega\right],$$

which is to say

$$a_0\omega(\omega_0 - \omega) + b_0\omega\Omega + a_0(\omega')^2 = b_0\Omega(\omega - \omega_0) + a_0\Omega^2 + a_0\omega_0(\omega_0 - \omega) + b_0\omega_0\Omega,$$

or

$$a_0\left[\omega\omega_0 - \omega^2 + (\omega')^2 - \Omega^2 - \omega_0^2 + \omega_0\omega\right] = b_0\left[\Omega\omega - \omega_0\Omega + \omega_0\Omega - \omega\Omega\right] = 0.$$

Substituting Eq. 9.91 for ω', the coefficient of a_0 on the left becomes

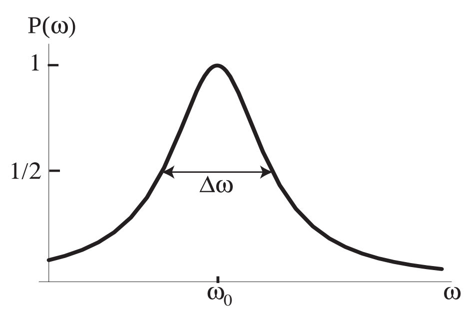
$$2\omega\omega_0 - \omega^2 + (\omega - \omega_0)^2 + \Omega^2 - \Omega^2 - \omega_0^2 = 0. \quad \checkmark$$

The check of $b(t)$ is identical, with $a \leftrightarrow b$, $\omega_0 \to -\omega_0$, and $\omega \to -\omega$.

(d)

$$b(t) = i\frac{\Omega}{\omega'}\sin(\omega' t/2)e^{-i\omega t/2}; \quad P(t) = |b(t)|^2 = \boxed{\left(\frac{\Omega}{\omega'}\right)^2\sin^2(\omega' t/2).}$$

(e)



The maximum ($P_{\max} = 1$) occurs (obviously) at $\omega = \omega_0$.

$P = \frac{1}{2} \Rightarrow (\omega - \omega_0)^2 = \Omega^2 \Rightarrow \omega = \omega_0 \pm \Omega$, so $\Delta\omega = \omega_+ - \omega_- = \boxed{2\Omega.}$

(f) $B_0 = 10,000$ gauss $= 1$ T; $B_{\rm rf} = 0.01$ gauss $= 1\times 10^{-6}$ T. $\omega_0 = \gamma B_0$. Comparing Eqs. 4.156 and 6.85, $\gamma = \dfrac{g_p e}{2m_p}$, where $g_p = 5.59$. So

$$\nu_{\rm res} = \frac{\omega_0}{2\pi} = \frac{g_p e}{4\pi m_p}B_0 = \frac{(5.59)(1.6\times 10^{-19})}{4\pi(1.67\times 10^{-27})}(1) = \boxed{4.26\times 10^7 \text{ Hz.}}$$

$$\Delta\nu = \frac{\Delta\omega}{2\pi} = \frac{\Omega}{\pi} = \frac{\gamma}{2\pi}2B_{\rm rf} = \nu_{\rm res}\frac{2B_{\rm rf}}{B_0} = (4.26\times 10^7)(2\times 10^{-6}) = \boxed{85.2 \text{ Hz.}}$$

Problem 9.21

(a)

$$H' = -q\mathbf{E}\cdot\mathbf{r} = -q(\mathbf{E}_0\cdot\mathbf{r})(\mathbf{k}\cdot\mathbf{r})\sin(\omega t). \quad \text{Write } \mathbf{E}_0 = E_0\hat{n},\ \mathbf{k} = \frac{\omega}{c}\hat{k}. \quad \text{Then}$$

$$H' = -q\frac{E_0\omega}{c}(\hat{n}\cdot\mathbf{r})(\hat{k}\cdot\mathbf{r})\sin(\omega t). \quad H'_{ba} = -\frac{qE_0\omega}{c}\langle b|(\hat{n}\cdot\mathbf{r})(\hat{k}\cdot\mathbf{r})|a\rangle\sin(\omega t).$$

This is the analog to Eq. 9.33: $H'_{ba} = -qE_0\langle b|\hat{n}\cdot\mathbf{r}|a\rangle\cos\omega t$. The rest of the analysis is identical to the dipole case (except that it is $\sin(\omega t)$ instead of $\cos(\omega t)$, but this amounts to resetting the clock, and clearly has no effect on the transition rate). We can skip therefore to Eq. 9.56, except for the factor of 1/3, which came from the averaging in Eq. 9.46:

$$A = \frac{\omega^3}{\pi\epsilon_0\hbar c^3}\frac{q^2\omega^2}{c^2}|\langle b|(\hat{n}\cdot\mathbf{r})(\hat{k}\cdot\mathbf{r})|a\rangle|^2 = \boxed{\frac{q^2\omega^5}{\pi\epsilon_0\hbar c^5}|\langle b|(\hat{n}\cdot\mathbf{r})(\hat{k}\cdot\mathbf{r})|a\rangle|^2.}$$

(b) Let the oscillator lie along the x direction, so $(\hat{n}\cdot\mathbf{r}) = \hat{n}_x x$ and $\hat{k}\cdot\mathbf{r} = \hat{k}_x x$. For a transition from n to n', we have

$$A = \frac{q^2\omega^5}{\pi\epsilon_0\hbar c^5}\left(\hat{k}_x\hat{n}_x\right)^2|\langle n'|x^2|n\rangle|^2. \quad \text{From Example 2.5,} \quad \langle n'|x^2|n\rangle = \frac{\hbar}{2m\bar{\omega}}\langle n'|(a_+^2 + a_+a_- + a_-a_+ + a_-^2)|n\rangle,$$

where $\bar{\omega}$ is the frequency of the *oscillator*, not to be confused with ω, the frequency of the electromagnetic *wave*. Now, for spontaneous emission the final state must be *lower* in energy, so $n' < n$, and hence the only surviving term is a_-^2. Using Eq. 2.66:

$$\langle n'|x^2|n\rangle = \frac{\hbar}{2m\bar{\omega}}\langle n'|\sqrt{n(n-1)}|n-2\rangle = \frac{\hbar}{2m\bar{\omega}}\sqrt{n(n-1)}\,\delta_{n',n-2}.$$

Evidently transitions only go from $|n\rangle$ to $|n-2\rangle$, and hence

$$\omega = \frac{E_n - E_{n-2}}{\hbar} = \frac{1}{\hbar}\left[(n+\tfrac{1}{2})\hbar\bar{\omega} - (n-2+\tfrac{1}{2})\hbar\bar{\omega}\right] = 2\bar{\omega}.$$

$$\langle n'|x^2|n\rangle = \frac{\hbar}{m\omega}\sqrt{n(n-1)}\,\delta_{n',n-2}; \quad R_{n\to n-2} = \frac{q^2\omega^5}{\pi\epsilon_0\hbar c^5}(\hat{k}_x\hat{n}_x)^2\frac{\hbar^2}{m^2\omega^2}n(n-1).$$

It remains to calculate the average of $(\hat{k}_x\hat{n}_x)^2$. It's easiest to reorient the oscillator along a direction $\hat{r}$, making angle θ with the z axis, and let the radiation be incident from the z direction (so $\hat{k}_x \to \hat{k}_r = \cos\theta$).

Averaging over the two polarizations ($\hat{\imath}$ and $\hat{\jmath}$): $\langle \hat{n}_r^2 \rangle = \frac{1}{2}\left(\hat{\imath}_r^2 + \hat{\jmath}_r^2\right) = \frac{1}{2}\left(\sin^2\theta\cos^2\phi + \sin^2\theta\sin^2\phi\right) = \frac{1}{2}\sin^2\theta$. Now average overall directions:

$$\langle \hat{k}_r^2 \hat{n}_r^2 \rangle = \frac{1}{4\pi}\int \frac{1}{2}\sin^2\theta\cos^2\theta\sin\theta\,d\theta\,d\phi = \frac{1}{8\pi}2\pi\int_0^\pi (1-\cos^2\theta)\cos^2\theta\sin\theta\,d\theta$$
$$= \frac{1}{4}\left[-\frac{\cos^3\theta}{3} + \frac{\cos^5\theta}{5}\right]\Big|_0^\pi = \frac{1}{4}\left(\frac{2}{3} - \frac{2}{5}\right) = \frac{1}{15}.$$

$$\boxed{R = \frac{1}{15}\frac{q^2\hbar\omega^3}{\pi\epsilon_0 m^2 c^5} n(n-1).} \quad \text{Comparing Eq. 9.63:} \quad \frac{R(\text{forbidden})}{R(\text{allowed})} = \boxed{\frac{2}{5}(n-1)\frac{\hbar\omega}{mc^2}.}$$

For a nonrelativistic system, $\hbar\omega \ll mc^2$; hence the term "forbidden".

(c) If both the initial state and the final state have $l = 0$, the wave function is independent of angle ($Y_0^0 = 1/\sqrt{4\pi}$), and the angular part of the integral is:

$$\langle a|(\hat{n}\cdot\mathbf{r})(\hat{k}\cdot\mathbf{r})|b\rangle = \cdots\int(\hat{n}\cdot\mathbf{r})(\hat{k}\cdot\mathbf{r})\sin\theta\,d\theta\,d\phi = \cdots\frac{4\pi}{3}(\hat{n}\cdot\hat{k}) \quad \text{(Eq. 6.95).}$$

But $\hat{n}\cdot\hat{k} = 0$, since electromagnetic waves are transverse. So $R = 0$ in this case, both for allowed and for forbidden transitions.

Problem 9.22

[This is done in Fermi's *Notes on Quantum Mechanics* (Chicago, 1995), Section 24, but I am looking for a more accessible treatment.]
