Atom-field Absorption & Emission Processes.

11) Now we turn to Topic III on p. QF1 -- calculation of transition amplitudes for the quantized atom - quantized field coupling. We have the interaction...

$$\rightarrow \mathcal{H}_{int} = -(q/mc)[\mathbb{A}\cdot\mathbb{p} + \mathbb{S}\cdot\mathbb{B}] \quad \int \mathbb{p}\ \&\ \mathbb{S} \text{ are momentum \& spin of } q \text{ in atom; } \mathbb{A}\ \&\ \mathbb{B} \text{ are rad}^{\underline{n}} \text{ fields,} \tag{58}$$

Which is accurate to $\mathcal{O}(\mathbb{A})$. Put in $\mathbb{A}$ of Eq. (46) & $\mathbb{B}$ of Eq. (52), and write:

$$\left.\begin{array}{l} \boxed{\mathcal{H}_{int} = \sum_{s,\sigma}\left[a_{s\sigma}\,\mathrm{J}(\mathbb{k}_s,\sigma) + a_{s\sigma}^{\dagger}\,\mathrm{J}^{\dagger}(\mathbb{k}_s,\sigma)\right]} \\ \text{w/}\quad \mathrm{J}(\mathbb{k}_s,\sigma) = -\frac{q}{mc}\left(\frac{2\pi\hbar c}{V k_s}\right)^{\frac{1}{2}} e^{i\mathbb{k}_s\cdot\mathbb{r}}\,\hat{\varepsilon}_{s\sigma}\cdot(\mathbb{p} + i\,\mathbb{S}\times\mathbb{k}_s) = \mathrm{J}_{s\sigma}. \end{array}\right\} \tag{59}$$

$\mathrm{J}_{s\sigma}$ has the dimensions of energy, and operates exclusively on atom coordinates.

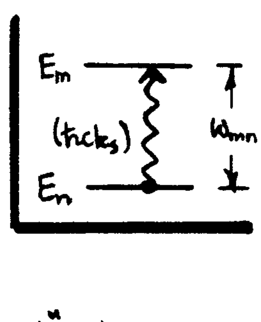
Now, per the theory sketch in Eqs. (12)-(14) and Eqs. (48)-(49), we are interested in transitions $n\rightarrow m$ for the atom, accompanied by $(N)\rightarrow(M)$ for the radiation field, which are governed by matrix elements of the form...

$$\langle m(M)|\mathcal{H}_{int}|n(N)\rangle = \sum_{s,\sigma}\Big[\underbrace{\langle(M)|a_{s\sigma}|(N)\rangle}_{\text{①, ABSORPTION}}\langle m|\mathrm{J}_{s\sigma}|n\rangle + \underbrace{\langle(M)|a_{s\sigma}^{\dagger}|(N)\rangle}_{\text{②, EMISSION}}\langle m|\mathrm{J}_{s\sigma}^{\dagger}|n\rangle\Big]. \tag{60}$$

Since the photon operators $a_{s\sigma}$ & $a_{s\sigma}^{\dagger}$ resp. annihilate & create one photon, it is clear that terms ① & ② describe resp. the absorption & emission of that photon by the atom. In detail, the energy transactions are...

①, **ABSORPTION**. $\langle(M)|a_{s\sigma}|(N)\rangle = \sqrt{N_{s\sigma}}$, if $\underline{M_{s\sigma} = N_{s\sigma} - 1}$ (and zero otherwise).

Rad$^{\underline{n}}$ field loses one photon @ energy $\hbar c k_s$; the atom absorbs it.



i.e./ $E_{n(N)}^{(s\sigma)} = E_n + N_{s\sigma}\hbar c k_s \rightarrow E_{m(M)}^{(s\sigma)} = E_m + (N_{s\sigma} - 1)\hbar c k_s$,

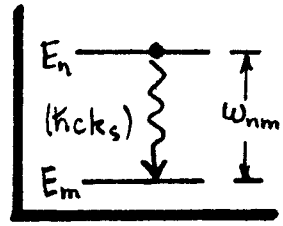
or/ $E_n = E_m - \hbar c k_s$, i.e./ $E_m = E_n + \hbar c k_s$, promoted. (61a)

So, if energy is conserved overall, the atom must absorb the "lost" photon.

Absorption & Emission of Single Photons by the Atom.

② EMISSION. $\langle(M)|a^{\dagger}_{s\sigma}|(N)\rangle = \sqrt{N_{s\sigma}+1}$, if $M_{s\sigma} = N_{s\sigma}+1$ (and zero otherwise).

Rad$^{\underline{n}}$ field gains one photon @ energy $\hbar c k_s$; the atom emits it.



i.e./ $E^{(s\sigma)}_{n(N)} = E_n + N_{s\sigma}\hbar c k_s \rightarrow E^{(s\sigma)}_{m(N)} = E_m + (N_{s\sigma}+1)\hbar c k_s$,

or/ $E_n = E_m + \hbar c k_s$, i.e./ $E_m = E_n - \hbar c k_s$, demoted. (61b)

Again, if energy is conserved, the atom must emit the "gained" photon.

Actually, energy conservation (to with the Uncertainty Principle, $\Delta E\Delta t \gtrsim \hbar$) will come out of the theory itself, as we will see later. So we are not invoking a Deus ex Machina here, when we claim energy conservation.

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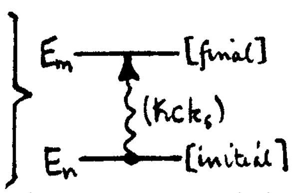
12) Although the theory can handle many single-photon processes going on together, we will be interested in just one at a time, where one photon in mode $(s\sigma)$ is absorbed or emitted. These one-photon processes are described by...

① ABSORPTION of Photon @ $(s\sigma)$: $E_n \rightarrow E_m = E_n + \hbar c k_s$;

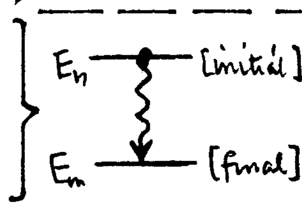
$$\langle m(M)|\mathcal{H}_{int}|n(N)\rangle_{abs.} = \sqrt{N_{s\sigma}}\,\langle m|J_{s\sigma}|n\rangle.$$



(62a)

② EMISSION of Photon @ $(s\sigma)$: $E_n \rightarrow E_m = E_n - \hbar c k_s$;

$$\langle m(M)|\mathcal{H}_{int}|n(N)\rangle_{ems.} = \sqrt{N_{s\sigma}+1}\,\langle m|J^{\dagger}_{s\sigma}|n\rangle.$$



(62b)

The operator $J_{s\sigma}$ is defined in Eq.(59); it gives the strength of $n\rightarrow m$ for the atom.

REMARKS on absorption/emission, per Eqs(62).

1. If no photons are present, $N_{s\sigma}=0$, then the absorption matrix element in (62a) vanishes... makes sense... the atom can't absorb a photon that doesn't exist. BUT the emission matrix element in (62b) does not vanish in the absence of photons. This suggests an atom can spontaneously emit a photon (consistent with energy cons$^{\underline{v}}$n).

REMARKS (cont'd)

This "spontaneous emission" or radiative decay process is a specific quantum effect -- the zero-point vibrations of the quantized field actually induce the decay. We shall look at this a bit later.

2. The matrix elements in Eqs.(62) describe single-photon transitions, since only first powers of the photon annihilation & creation operators a_{ks} & $a_{ks}^{\dagger}$ were used. Had we carried along the $\mathbb{A}^2$ term in $\mathcal{H}_{EM}$ of Eq.(5), we would have gotten second powers of the a's, like aa, $aa^{\dagger}$, etc. Acting on the radiation field, such operators would annihilate two photons, or create & annihilate a photon, etc. Such double-photon processes (e.g. Raman effect) must be accounted for when the radiation field is intense... e.g. when the atom is irradiated by a laser. Then the bookkeeping for transitions gets ~ complicated.

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13) With the atom-field matrix elements of $\mathcal{H}_{int}$ specified by Eqs (62), it is ~ easy to do perturbation theory on the interaction amplitudes of Eq. (14). In first order...¶

$$\rightarrow i\hbar\,\dot{C}^{(1)}_{f(F)} = \sum_{n(N)} C^{(0)}_{n(N)} \langle f(F)|\mathcal{H}_{int}|n(N)\rangle e^{\frac{i}{\hbar}(E_{f(F)}-E_{n(N)})t}, \qquad (63)$$

for the amplitude of a final state $f(F)$. Choose as an initial condition the atom+field in a "pure" state $\iota(I)$, i.e.

$$\text{CHOOSE: } C^{(0)}_{\iota(I)} = 1, \text{ and all other } C^{(0)}_{n(N)} \equiv 0. \qquad (64)$$

Then the amplitude for $\iota(I)\rightarrow f(F)$ via $\mathcal{H}_{int}$ is -- to first order in $\mathcal{H}_{int}$:

$$i\hbar\,\dot{C}^{(1)}_{f(F)} = \langle f(F)|\mathcal{H}_{int}|\iota(I)\rangle e^{\frac{i}{\hbar}(E_{f(F)}-E_{\iota(I)})t}, \quad \int \quad \underline{\text{NOTE: } \langle\mathcal{H}_{int}\rangle \text{ is t-indep}^t}$$

$$\xrightarrow{\text{Soln}} C^{(1)}_{f(F)}(t) - \cancelto{0}{C^{(1)}_{f(F)}(t_0)} = \langle f(F)|\mathcal{H}_{int}|\iota(I)\rangle \frac{e^{\frac{i}{\hbar}(E_{f(F)}-E_{\iota(I)})t_0} - e^{\frac{i}{\hbar}(E_{f(F)}-E_{\iota(I)})t}}{(E_{f(F)}-E_{\iota(I)})}. \qquad (65)$$

t_0 is a time such that $\mathcal{H}_{int}$ is negligible (e.g. not yet turned on) for $t<t_0$. It is convenient to set $t_0=0$. Also, we shall look at transitions $\iota(I)\rightarrow f(F)$ for

(next page)

¶ Same as first step in time-dependent perturbation theory. See class notes, p. tD4.

Single-photon absorption & emission probabilities (lowest-order).

which the initial & final states are <u>different</u>, so we set $C^{(1)}_{f(F)}(t_0)=0$. Then (65) is:

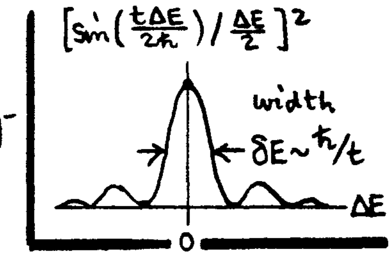
$$C^{(1)}_{f(F)}(t) = \langle f(F)|\mathcal{H}_{int}|\iota(I)\rangle \left[1-e^{\frac{i}{\hbar}(E_{f(F)}-E_{\iota(I)})t}\right]/(E_{f(F)}-E_{\iota(I)}),$$

So

$$\boxed{|C^{(1)}_{f(F)}(t)|^2 = |\langle \mathcal{F}|\mathcal{H}_{int}|\mathcal{I}\rangle|^2 \frac{\sin^2\frac{1}{\hbar}(\Delta E_{\mathcal{F}\mathcal{I}}/2)t}{(\Delta E_{\mathcal{F}\mathcal{I}}/2)^2}}$$

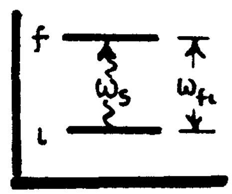
w/ $\mathcal{I}$ = initial state $\iota(I)$, $\mathcal{F}$ = final state $f(F)$; $\Delta E_{\mathcal{F}\mathcal{I}} = E_{\mathcal{F}} - E_{\mathcal{I}}$. (66)

$|C^{(1)}_{f(F)}(t)|^2$ is the $\iota(I)\to f(F)$ transition probability, to lowest order, for atom $\leftrightarrow$ field transitions driven by $\mathcal{H}_{int}$. As a fcn of the $\mathcal{I}$-$\mathcal{F}$ energy difference $\Delta E_{\mathcal{F}\mathcal{I}}$, it is strongly peaked in the neighborhood of $\Delta E_{\mathcal{F}\mathcal{I}}=0$, which implies <u>energy consvn</u>. The width $\delta E\sim\hbar/t$ is consistent with the energy uncertainty associated with a transition over a finite coupling time t.



With the matrix elements of Eqs (62), the two types of transition are:

① <u>ABSORPTION of one photon in mode $(s\sigma)$.</u>



$$E_{f(F)} - E_{\iota(I)} = [E_f + (N_{s\sigma}-1)\hbar c k_s] - [E_i + N_{s\sigma}\hbar c k_s]$$

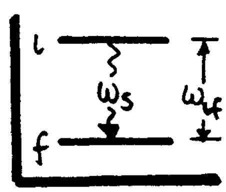
$$= \hbar(\omega_{fi}-\omega_s) \begin{cases} \omega_{fi} = (E_f-E_i)/\hbar, \text{ atom transition freq.;} \\ \omega_s = ck_s, \text{ frequency of } \underline{\text{absorbed}} \text{ photon.}\end{cases}$$

and

$$|C^{(1)}_{f(F)}(t)|^2_{abs.} = \frac{4}{\hbar^2} N_{s\sigma} |\langle f|J_{s\sigma}|\iota\rangle|^2 \sin^2\tfrac{1}{2}(\omega_{fi}-\omega_s)t/(\omega_{fi}-\omega_s)^2. \quad (67a)$$

There is strong peaking @ $\omega_f = \omega_i + \omega_s$, which is <u>why</u> this is an absorption.

② <u>EMISSION of one photon in mode $(s\sigma)$.</u>



$$E_{f(F)} - E_{\iota(I)} = [E_f + (N_{s\sigma}+1)\hbar c k_s] - [E_i + N_{s\sigma}\hbar c k_s]$$

$$= \hbar(\omega_s-\omega_{if}) \begin{cases} \omega_{if} = (E_i-E_f)/\hbar, \text{ atom transition freq.;} \\ \omega_s = ck_s, \text{ frequency of } \underline{\text{emitted}} \text{ photon.}\end{cases}$$

$$|C^{(1)}_{f(F)}(t)|^2_{ems.} = \frac{4}{\hbar^2}(N_{s\sigma}+1)|\langle f|J^{\dagger}_{s\sigma}|\iota\rangle|^2 \sin^2\tfrac{1}{2}(\omega_{if}-\omega_s)t/(\omega_{if}-\omega_s)^2. \quad (67b)$$

The strong peaking @ $\omega_f = \omega_i - \omega_s$ explains <u>why</u> this is an atomic emission.

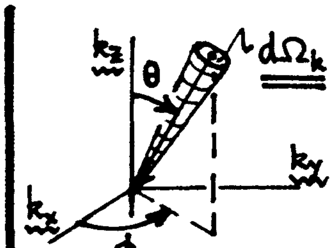
Move from a discrete to a continuous photon spectrum..

14) The $|C|^2$ in Eqs(67) give the desired transition probabilities for absorption or emission of single photons in mode $s\sigma$ during an atomic transition $i \to f$. But the atom rarely, if ever, finds itself in a monochromatic radiation field, w/ photons at just one frequency ω_s (exception: laser irradiation). So now we must learn to sum the $|C|^2$ over a distribution of photon $\mathbf{k}_s$-values.

The distribution of photon states is represented by the $N_{s\sigma}$, i.e. the number of photons in the modes $(s\sigma)$ in the initial radiation field. In practice, $N_{s\sigma}$ is a quasi-continuous distribution fcn $N_\sigma(k)$, which is proportional to the radiation intensity (i.e. total # photons) at wavenumber k and polarization σ. For example, $N_\sigma(k)$ could be the intensity distribution for blackbody radiation at temperature T [see footnote, p. QF8]. Another factor governing photon states is the # modes available (and consistent with boundary conditions) for a given k... we have touched on that question in Eq.(42), p. QF 13. Finally, we realize that it is not sufficient just to quote $k = |\mathbf{k}|$ to specify a photon; one can distinguish photons with the same k which propagate in different directions $\hat{k}$, and/or with different polarizations σ.

The photon mode availability factor is essentially geometric, and can be taken into account by a density-of-states fcn $\rho(k)$, such that:

$\rightarrow \rho(k)\,dk$ = # photon modes available in k to $k+dk$. (68)



$d\Omega_k = \sin\theta\, d\theta\, d\phi$ (in 3D $\mathbf{k}$-space)

For isotropic radiation (i.e. the free radiation field), obeying periodic boundary conditions (in an arbitrarily large "box" of vol. V), the # modes available in volume d^3k of 3D $\mathbf{k}$-space is $[V/(2\pi)^3]\,d^3k$, by Eq.(42), so the mode counting goes as

$$\sum_{\mathbf{k}} \rightarrow [V/(2\pi)^3]\int d^3k = \int_{4\pi} d\Omega_k \int_0^\infty \rho(k)\,dk, \text{ w/ } \rho(k) = Vk^2/(2\pi)^3. \quad (69)$$

This is a paraphrase of the discrete → continuous summation mentioned in Eq.(43).

Absorption & Emission Probabilities summed over a photon spectrum.

15) Now we can handle absorption / emission probabilities for atomic transitions $i \to f$ summed over distributions of photon states $N_\sigma(k)$. The sums are $\sum_{s,\sigma}$ on the Eq. (67) probabilities $|C_{f(F)}^{(1)}(t)|^2_{abs./ems.}$. Now $\sum_s$ means $\sum_{\mathbf{k}}$, in the sense of Eq. (69), and we shall denote these sums by

sum over photon polarizations, integration over solid ∡ for **k**.

$$\rightarrow \left[\sum_{s,\sigma} = \sum_{\sigma,4\pi}\int_0^\infty \rho(k)\,dk\,, \quad \text{w/} \quad \underline{\underline{\sum_{\sigma,4\pi} = \sum_\sigma \int_{4\pi} d\Omega_k}} \right. \qquad (70)$$

The summed absorption probability $P^{abs.}_{f>i}(t) = \sum_{s,\sigma} |C_{f(F)}^{(1)}(t)|^2_{abs.}$ is then...

$$\rightarrow \underline{P^{abs}_{f>i}(t) = \frac{1}{\hbar^2}\sum_{\sigma,4\pi}\int_0^\infty \rho(k)\,dk \cdot N_\sigma(k)\,|\langle f|J_\sigma(\mathbf{k})|i\rangle|^2\, \frac{\sin^2\frac{1}{2}(\omega_{fi}-ck)t}{\left[\frac{1}{2}(\omega_{fi}-ck)\right]^2}}. \qquad (71a)$$

And the summed emission probability is, similarly...

$$\rightarrow \underline{P^{ems}_{f<i}(t) = \frac{1}{\hbar^2}\sum_{\sigma,4\pi}\int_0^\infty \rho(k)\,dk \cdot [N_\sigma(k)+1]\,|\langle f|J^\dagger_\sigma(\mathbf{k})|i\rangle|^2\, \frac{\sin^2\frac{1}{2}(\omega_{if}-ck)t}{\left[\frac{1}{2}(\omega_{if}-ck)\right]^2}}. \qquad (71b)$$

The notation $f \gtrless i$ here means $\omega_f \gtrless \omega_i$.

The integrands in Eqs. (71) have strongly peaked fcns $\sin^2(t\frac{\Delta\omega}{2})/(\frac{\Delta\omega}{2})^2$ which dominate the k variation. These fcns represent <u>energy conservation</u> for the atom + field system, and their presence demands that the major contribution to the transition probabilities comes when: $\hbar ck\,[\text{photon}] \simeq \hbar|\omega_{fi}|\,[\text{atom}]$. We then "handle" the integrals by claiming that the k-variation of $\rho(k)$, $N_\sigma(k)$ and the matrix elements $|\langle f|J_\sigma(\mathbf{k})|i\rangle|^2$ is ~ slow compared the $\sin^2$ factors, and we evaluate them at $k_{fi} = \omega_{fi}/c$ (or $k_{if} = \omega_{if}/c$ in (71b)) and take them outside the integral. Procedure is the same for P^{abs} or P^{ems}. For the former:

$$\rightarrow P^{abs}_{f>i}(t) = \frac{1}{\hbar^2}\sum_{\sigma,4\pi}[N_\sigma(k_{fi})]\,|\langle f|J_\sigma(\mathbf{k}_{fi})|i\rangle|^2\,\rho(k_{fi})\int_0^\infty \frac{\sin^2\frac{1}{2}(\omega_{fi}-ck)t}{\left[\frac{1}{2}(\omega_{fi}-ck)\right]^2}\,dk. \qquad (72)$$

w/ $\underline{\hbar c k_{fi}\,[\text{photon}] = (E_f - E_i)\,[\text{atom}]}$; defines k_{fi}.

Change integration variables to: $x = \frac{1}{2}(ck-\omega_{fi})t$, so the integral in (72) is...

Transition probabilities per unit time for absorption & emission.

$$\left[\begin{array}{l}\int_0^\infty [\text{in Eq.(72)}]\,dk = \frac{2t}{c}\int_{-x_0}^{\infty}\left(\frac{\sin^2 x}{x^2}\right)dx = \frac{2\pi t}{c}\Big[1-\underbrace{\frac{1}{\pi}\int_{x_0}^{\infty}\frac{\sin^2 x}{x^2}\,dx}_{\text{call this }\eta(x_0)}\Big],\\ \text{w/ } \underline{\underline{x_0 = \tfrac{1}{2}\omega_{fi}t}}.\end{array}\right. \qquad (73)$$

The "leftover" integral $\eta(x_0)$ is a nuisance -- it gives an unwanted extra t-dependence in the problem. We can get rid of $\eta(x_0)$ by a somewhat restrictive assumption: we are only interested in the transition behavior at "long times", i.e. times for which $\boxed{t \gg 1/\omega_{fi}}$ (t = many Bohr orbit periods).¶ Then $x_0 \gg 1$, and $\eta(x_0) \to 0$, so (73) $\Rightarrow \int_0^\infty [\text{in Eq.(72)}]\,dk \to 2\pi t/c$. We use this in Eq.(72) to form the <u>transition probability per unit time for absorptions</u> $i \to f > i$:

$$\boxed{\Gamma_{f>i}^{(A)} = \frac{1}{t}P_{f>i}^{abs}(t) = \sum_{\sigma,4\pi}\left\{\frac{2\pi}{\hbar}\left[\frac{N_\sigma(k_{fi})}{\hbar c}|\langle f|J_\sigma(\mathbb{k}_{fi})|i\rangle|^2\right]\rho(k_{fi})\right\}.} \qquad (74)$$

This result could have been <u>anticipated</u>... the { } on the RHS is just <u>Fermi's Golden Rule</u> [class notes, p. tD 29]. However, had we tried using the Golden Rule at the outset, we would have had a difficult time identifying the right transition matrix element for $i \to f$ (atom), and we would have missed the quantum aspects of the radiation field. The latter are new and important.

A similar treatment of the emission process leads to:

$$\boxed{\Gamma_{f<i}^{(E)} = \frac{1}{t}P_{f<i}^{ems}(t) = \sum_{\sigma,4\pi}\left\{\frac{2\pi}{\hbar}\left[\frac{N_\sigma(k_{if})+1}{\hbar c}|\langle f|J_\sigma^\dagger(\mathbb{k}_{if})|i\rangle|^2\right]\rho(k_{if})\right\}.} \qquad (75)$$

w/ $\underline{\underline{\hbar c k_{if}\,[\text{photon}] = (E_i - E_f)\,[\text{atom}]}}$; defines k_{if}. (NOTE: $t \gg 1/\omega_{if}$, as above).

The Γ's in Eqs. (74) & (75) are called "<u>transition rates</u>", and they measure the # (atomic) transitions $i \to f$ per unit time in the presence of a photon field $N_\sigma(k)$.

¶ More precisely: $t \gg 2/\omega_{fi} = \lambda_{fi}/\pi c$, for a (absorbed) photon @ wavelength λ_{fi}. At optical wavelengths, $\lambda \sim 5000\,\text{Å}$, requires: $t \gg 5\times10^{-16}$ sec. Restrictive? More, later.

Interlude: What we have done, and where we can go from here.

16) We now have the major working parts of fully quantized theory of an atom interacting with a radiation field. In quantizing the field via a SHO scheme [Eqs. (15)-(57)], we have had major sucesses in explaining "photons" as the natural quanta of the EM field, and in accounting for atom + field interactions in terms of absorption & emission of these photons ($\sim$ tuned to the atomic transition frequencies: $\omega[\text{photon}] \simeq \frac{1}{\hbar}|E_i - E_f|[\text{atom}]$). The transition rates Γ in Eqs. (74) & (75) for absorption & emission tell most of the story.

The field quantization has, however, suggested some major problems... the vacuum state $|0\rangle$ of the field has a zero-point energy ($\frac{1}{2}\hbar\omega$ in each mode, in the absence of photons in that mode), which invests the vacuum with an infinite energy over all modes [see footnote on p. QF8]. Furthermore, the EM fields $\mathbb{E}$ & $\mathbb{B}$ are now non-commuting operators. This is a mixed blessing... the photon itself now behaves like a standard QM particle obeying a position-momentum uncertainty relation (remark #2 on p. QF16), but the field vacuum state $|0\rangle$ picks up very large zero-point fluctuations in the fields [Eq. (56)]. So the sucesses of field-quantization-via-photons have been bought at the expense of filling up the hitherto innocuous vacuum with fields possessing ∞ energy and showing arbitrarily large fluctuations. So-called "renormalization" techniques have been invented to get rid of these embarrassments, but Dirac went to his grave thinking the whole theory stank.

Still, we can do some orthodox things with parts of the theory that work. E.g.

(A) Evaluate (i.e. reduce) the matrix elements of $J_\sigma(\mathbb{k})$ & $J_\sigma^\dagger(\mathbb{k})$ in Eqs (74) & (75).

(B) Analyse the "spontaneous emission" case, i.e. $N_\sigma(k_{if}) \equiv 0$ in Eq. (75).

(C) Remove the time restriction $t \gg 1/|\omega_{fi}|$ in the Γ's of Eq. (74) & (75).

Topics (A) & (B) are $\sim$ straightforward. (C) is much more difficult, because it is connected with radiation reaction & radiative level (Lamb) shifts.