Simplifying the transition rate Γ's.

17) We can write the transition rate Γ's of Eqs. (74) & (75) in a more appealing form. Plug in the operator $J_{s\sigma}$ of Eq. (59), remembering that the $\sum_s$ has been done [as an integral over k, per Eq. (70)]. Put $\rho(k) = Vk^2/(2\pi)^3$ for the photon density of states [Eq. (69)], and drop clumsy subscripts on k. Then...

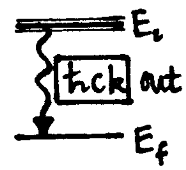
① $$\Gamma^{(A)}_{f \leftarrow i} = \left(\frac{q}{mc}\right)^2 \frac{k}{2\pi\hbar} \sum_{\sigma, 4\pi} [N_\sigma(k)] \left| \hat{\varepsilon}_\sigma \cdot \langle f | \mathbb{M}(\mathbb{k}) | i \rangle \right|^2,$$

w/ $\hbar ck = E_f - E_i$, for **ABSORPTION**; (76)

in $\boxed{\hbar ck}$

② $$\Gamma^{(E)}_{f \leftarrow i} = \left(\frac{q}{mc}\right)^2 \frac{k}{2\pi\hbar} \sum_{\sigma, 4\pi} [N_\sigma(k) + 1] \left| \hat{\varepsilon}_\sigma \cdot \langle f | \mathbb{M}^\dagger(\mathbb{k}) | i \rangle \right|^2$$

w/ $\hbar ck = E_i - E_f$, for **EMISSION**; (77)



→ where: $$\mathbb{M}(\mathbb{k}) = e^{i\mathbb{k}\cdot\mathbb{r}}(\mathbb{p} + i\,\mathbb{S} \times \mathbb{k}). \tag{78}$$

Notice that the volume V [introduced in Eq. (19) as the radiation field container, and used in Eq. (42) for counting photon modes] has cancelled out ($\frac{1}{V}$ in $\langle J_\sigma \rangle^2$ against V in $\rho(k)$). This makes our calculation independent of V, as it should be. Still left in the above Γ's is the sum $\sum_{\sigma, 4\pi}$, which is a sum over the photon polarization states $\sigma = 1, 2$, and the 4π solid ∡ for $\mathbb{k}$ [Eqs. (69)-(70)].

For a free radiation field, the photon # $N_\sigma(k) = N(k)$ is independent of polarization, in which case we can take it outside the sum $\sum_{\sigma, 4\pi}$, and write...

$$\Gamma^{(A)}_{f \leftarrow i} = [N(k)] \left(\frac{q}{mc}\right)^2 \frac{k}{2\pi\hbar} \sum_{\sigma, 4\pi} \left| \hat{\varepsilon}_\sigma \cdot \langle f | \mathbb{M} | i \rangle \right|^2, \tag{79a}$$

$$\Gamma^{(E)}_{f \leftarrow i} = [N(k) + 1] \left(\frac{q}{mc}\right)^2 \frac{k}{2\pi\hbar} \sum_{\sigma, 4\pi} \left| \hat{\varepsilon}_\sigma \cdot \langle f | \mathbb{M}^\dagger | i \rangle \right|^2. \tag{79b}$$

Clearly $\Gamma^{(A)}_{f \leftarrow i}$ is a wholly induced process, in that there is no absorption possible when there is no external field present (i.e. $N(k) = 0$). By contrast, $\Gamma^{(E)}_{f \leftarrow i}$ has an induced part plus a spontaneous part which is nonzero even w/o a field.

Relations between the rates Γ. Detailed Balancing.

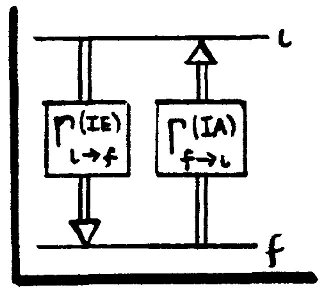
18) Split the emission Γ of Eq. (79b) into two parts...

$$\rightarrow \underline{\underline{\Gamma^{(E)}_{f\leftarrow i} = \Gamma^{(SE)}_{f\leftarrow i} + \Gamma^{(IE)}_{f\leftarrow i}}} \quad \int^{w/} \underline{\Gamma^{(SE)}_{f\leftarrow i} = \left(\frac{q}{mc}\right)^2 \frac{k}{2\pi\hbar} \sum_{\sigma,4\pi} |\hat{\varepsilon}_\sigma \cdot \langle f|\mathbb{M}^\dagger|i\rangle|^2}, \text{ spontaneous emission rate;}$$

$$\text{and: } \Gamma^{(IE)}_{f\leftarrow i} = N(k)\,\Gamma^{(SE)}_{f\leftarrow i}, \text{ induced emission rate.} \quad (80)$$

We now have the spontaneous (no radiation field present) and induced (field present: $N(k)>0$) emission rates separated. Next, we note that since...

$$\rightarrow |\langle f|\mathbb{M}^\dagger|i\rangle|^2 = |\langle i|\mathbb{M}|f\rangle|^2 \Rightarrow \underline{\underline{\Gamma^{(IE)}_{i\to f} = \Gamma^{(IA)}_{f\to i}}}. \quad (81)$$



... then, in the presence of a radiation field [$N(k)>0$ at the appropriate $k=(E_i-E_f)/\hbar c$], the induced emission rate for $i\to f$ is exactly matched by the induced absorption rate for $f\to i$, as indicated by the sketch. The radiation field, when present, acts impartially -- it drives just as many emissions $i\to f$ as absorptions $f\to i$. This is called "detailed balancing", a necessary thermodynamic feature of our theory.

The spontaneous emission rate $\Gamma^{(SE)}_{f\leftarrow i}$ is a different (and new) breed. It says that whenever an initial state $|i\rangle$ is connected to a lower-lying final state $\langle f|$ via the matrix element $\langle f|\mathbb{M}^\dagger|i\rangle$, $\mathbb{M}$ in Eq. (78), then $|i\rangle$ will spontaneously decay to $\langle f|$, w/o any external field present. So it says that any excited state of an "atom" (more generally any QM system with bound states) will normally decay to the ground state -- if it is capable of emitting a photon to carry off the energy $(E_i-E_f)=\hbar ck$.*

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* $\langle f|\mathbb{M}^\dagger|i\rangle$, which is a first order approx^n for the $i\to f$ emission, may vanish. However, in higher orders of perturb^n theory, it is ~always possible to find a coupling (which may involve intermediate states) $\langle f|(\text{something})|i\rangle$ which provides $\Gamma^{(SE)}_{f\leftarrow i}>0$.

The nature of the spontaneous decay rate $\Gamma^{(SE)}_{f>i}$.

Where did the spontaneous decay rate $\Gamma^{(SE)}_{f<i}$ come from? Precisely from the quantization of the radiation field via the SHO notion, and specifically from the fact that the photon creation operator $a^\dagger$ obeys: $a^\dagger|N\rangle = \sqrt{N+1}\,|N+1\rangle$ [see Eq. (29), and the emission process in Eq. (62b)]. The "1" in the $\sqrt{N+1}$ here is what ultimately gives $\Gamma^{(SE)}_{f<i}$, so it a peculiarly QM effect, and we would have missed it w/o quantizing the field. Fermi might have missed it.

What triggers $\Gamma^{(SE)}_{f<i}$, i.e. what "tickles" the atom into a spontaneous emission $i \to f$ with no external field present? (Equivalently -- why doesn't the atom remain indefinitely in a metastable state @ $i > f$?). The answer is connected with the nature of the vacuum state $|0\rangle$ of the quantized field. The matrix element $\langle 1|a^\dagger|0\rangle$ is nonzero during a spontaneous emission [cf. Eqs. (60) & (62b)], i.e. the initial state of the atom + field is: atom in excited state i and field in vacuum $|0\rangle$. But the $|0\rangle$ state of the field is filled with large fluctuating $\mathbb{E}$-fields [Eq. (56)], and a uniform distribution of zero-point "half" photons $\frac{1}{2}\hbar ck$ [p. QF8]. In the former case, the $\mathbb{E}$-field fluctuations can "tickle" the atom state i into giving up its metastability, and doing the emission $i \to f$. In the latter case, two "half" photons (at k-values close together) can combine to form a virtual photon @ $\hbar ck \simeq (E_i - E_f)$ which will induce the emission $i \to f$; this process is permissible when the "virtual" photon exists for a time which is "inside" the uncertainty principle, i.e. $\Delta t < \hbar/(E_i - E_f)$*; since such a photon "violates" the energy-time inequality, it will never be seen -- that's why it is called a "virtual" photon. Anyway, the vacuum field $|0\rangle$ provides ample opportunity to "induce" the spontaneous decay $i \to f$

> The discovery of $\Gamma^{(SE)}_{f>i}$ is another major success of the theory [see p. QF25].

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* Notice: this Δt lies inside the times ignored in Eq. (73). Very interesting...

Spontaneous decay rate Γ in dipole approximation.

19) It is clear from Eqs. (80) & (81) that the key transition rate to calculate is $\Gamma^{(SE)}_{i\to f}$, since the induced rates are: $\Gamma^{(IE)}_{i\to f} = \Gamma^{(IA)}_{f\to i} = N(k)\,\Gamma^{(SE)}_{i\to f}$. We drop the sub- and superscripts and thus look at...

$$\rightarrow \underline{\Gamma^{(SE)}_{f<i} = \Gamma = (q/mc)^2 \frac{k}{2\pi\hbar} \sum_{\sigma,4\pi} |\hat{\varepsilon}_\sigma \cdot \langle f|\mathbb{M}^\dagger|i\rangle|^2}. \qquad (82)$$

The atom operator $\mathbb{M}$ is defined in Eq. (78), viz.

$$\rightarrow \mathbb{M} = e^{i\mathbf{k}\cdot\mathbf{r}}(\mathbf{p} + i\,\mathbb{S}\times\mathbf{k}), \qquad (83)$$

and we shall do a "<u>dipole</u> <u>approximation</u>" on the matrix element in (82). This mainly amounts to claiming the phase $\mathbf{k}\cdot\mathbf{r} \ll 1$ for a typical "atom", so that $e^{i\mathbf{k}\cdot\mathbf{r}} \rightarrow 1$ in (83). Generically, this is the claim that $\underline{\mathbf{k}\cdot\mathbf{r} \sim 2\pi(d/\lambda) \ll 1}$, the size d of the radiating system is small compared to the radiated wavelength λ (and $d \ll \lambda$ is called the dipole approxn in classical EM). For an actual (hydrogenlike) atom...

$$\rightarrow \mathbf{k}\cdot\mathbf{r} \sim \left(\frac{E_i - E_f}{\hbar c}\right) a_0 \sim \left(\frac{\frac{1}{2}(Z\alpha)^2 mc^2}{\hbar c}\right)\frac{\hbar^2}{Zme^2} = \frac{1}{2}(Z\alpha) \ll 1, \qquad (84)$$

... so $\mathbf{k}\cdot\mathbf{r} \ll 1$ is explicitly a good approxn. For the same atom, the of the $\mathbb{S}\times\mathbf{k}$ and $\mathbf{p}$ terms in (83) goes as...

$$\rightarrow |\mathbb{S}\times\mathbf{k}|/|\mathbf{p}| \sim \tfrac{1}{2}\hbar k/mcZ\alpha \sim \frac{1}{4}(Z\alpha) \ll 1, \qquad (85)$$

... and we shall also drop the term in $\mathbb{S}$. This leaves $\mathbb{M} \simeq \mathbf{p}$, and so the spontaneous emission rate in (82) is -- to leading order

$$\left[\!\left[\, \Gamma = (q/mc)^2 \frac{k}{2\pi\hbar} \sum_{\sigma,4\pi} |\hat{\varepsilon}_\sigma \cdot \langle f|\mathbf{p}|i\rangle|^2 \,\right]\!\right]. \qquad (86)$$

This version of Γ gives the <u>electric</u> <u>dipole</u> <u>radiation</u> from the atom. The term in $\mathbb{S}$ just dropped would give the magnetic dipole radiation, and the higher order terms in $e^{i\mathbf{k}\cdot\mathbf{r}} = 1 + i(\mathbf{k}\cdot\mathbf{r}) + \ldots$ would give quadrupole, etc. radiation.

Reduction of spontaneous decay rate Γ (in dipole approxn).

20) By the atom's QM eqtn-of-motion [Sakurai Eq. (2.2.19)]

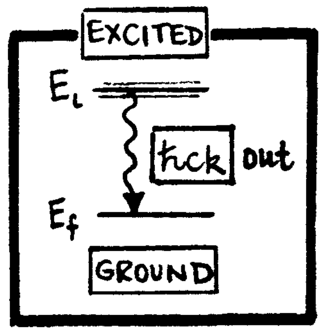
$$\rightarrow \mathbf{p} = m\frac{d\mathbf{r}}{dt} \rightarrow \frac{im}{\hbar}[\mathcal{H}_S, \mathbf{r}], \quad \mathcal{H}_S = \text{Schrodinger Ham}^{\text{n}}\ [\text{Eq. }(6)],$$

so/ $$\langle f|\mathbf{p}|i\rangle = \frac{im}{\hbar}\left(\langle f|\mathcal{H}_S\mathbf{r}|i\rangle - \langle f|\mathbf{r}\,\mathcal{H}_S|i\rangle\right)$$

$$= \frac{im}{\hbar}\underbrace{(E_f - E_i)}_{=(-)\hbar ck,\ \text{for emitted photon.}}\langle f|\mathbf{r}|i\rangle = -imck\,\langle f|\mathbf{r}|i\rangle. \qquad (87)$$

Then, in Eq (86)...

$$\left[\begin{array}{l} \Gamma = (k^3/2\pi\hbar)\sum_{\sigma,4\pi}|\hat{\epsilon}_\sigma\cdot\mathbf{D}_{fi}|^2 \\ \text{w/}\ \hbar ck\,[\text{photon}] = (E_i - E_f)\,[\text{atom}], \\ \text{&/}\ \mathbf{D}_{fi} = \langle f|q\mathbf{r}|i\rangle \ \Big\} \text{ electric dipole moment for (transition) } i\to f. \end{array}\right. \qquad (88)$$



The remaining sum, $\sum_{\sigma,4\pi}$, over polarizations σ and directions $\int_{4\pi}d\Omega_k$ for $\mathbf{k}$ [see Eq. (70)] is straightforward (details in footnote ¶ below). The result is...

$$\boxed{\Gamma = (4k^3/3\hbar)\,|\langle f|q\mathbf{r}|i\rangle|^2}, \ \text{w/}\ \hbar ck\left[\begin{smallmatrix}\text{emitted}\\ \text{photon}\end{smallmatrix}\right] = (E_i - E_f)\left[\begin{smallmatrix}\text{atomic}\\ \text{transition}\end{smallmatrix}\right]. \qquad (89)$$

This is a Basic Result for the theory: it is the (leading order) dipole approxn for an atom's spontaneous emission rate in a decay from initial excited state $|i\rangle$ to a lower-lying state $\langle f|$. It is summed over photon polarizations, and averaged over photon directions.

¶ $\sum_\sigma|\hat{\epsilon}_\sigma\cdot\mathbf{D}|^2 = \sum_{i,j}D_iD_j^\dagger\left(\sum_\sigma\epsilon_{\sigma i}\,\epsilon_{\sigma j}\right) = |\mathbf{D}|^2 - \frac{1}{k^2}\sum_{i,j}D_iD_j^\dagger\,k_ik_j$, by Eq. (45b).

So $\sum_{\sigma,4\pi}|\hat{\epsilon}_\sigma\cdot\mathbf{D}|^2 = 4\pi\left\{|\mathbf{D}|^2 - \sum_{i,j}D_iD_j^\dagger\left[\frac{1}{4\pi k^2}\int_{4\pi}d\Omega_k\,k_ik_j\right]\right\} = 4\pi|\mathbf{D}|^2\left\{1 - \frac{1}{3}\right\}$.

i.e./ $\boxed{\sum_{\sigma,4\pi}|\hat{\epsilon}_\sigma\cdot\mathbf{D}|^2 = \frac{8\pi}{3}|\mathbf{D}|^2}$, for any vector $\mathbf{D}$ independent of $\hat{k}$.

Remarks on Γ: size estimate, higher-order terms, $\iota \to \{f\}$.

REMARKS on decay rate Γ of Eq.(89).

1. For a "typical" atomic transition in a hydrogenlike atom, take...

transition energy: $\hbar ck = \eta \cdot \frac{1}{2} mc^2 (Z\alpha)^2$, η a numerical factor $(0<\eta<1)$;

transition dipole moment: $|\langle f|e\mathbf{r}|\iota\rangle| = \mu e a_0/Z$, $0<\mu<1$;

So//
$$\Gamma = \frac{1}{6}\eta^3 \mu^2 (Z\alpha)^4 / (a_0/c). \tag{90}$$

$a_0/c = 1.76\times 10^{-19}$ sec is the characteristic time for a photon to travel across a system of atomic dimension $\sim a_0$. For $\eta = 0.2$ (corresponding to a photon at wavelength $\lambda = (4560\,\text{Å})/Z^2$), and $\mu \simeq 1$: $\Gamma \simeq 2.15\, Z^4 \times 10^7\ \text{sec}^{-1}$. So $\iota \to f$ rapidly... the lifetime of ι is only $\tau = 1/\Gamma \simeq 4.65\times 10^{-8}/Z^4$, sec.

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2. Γ vanishes when the electric dipole matrix element $\langle f|e\mathbf{r}|\iota\rangle$ vanishes; this will always happen when states $|\iota\rangle$ & $\langle f|$ have the same parity. In this case $|\iota\rangle$ may decay to a different state $\langle f'|$, of opposite parity. Or a non-vanishing Γ can be found by magnetic dipole coupling $\iota \to f$, or higher-order multipoles (see footnote on p. QF 27).*

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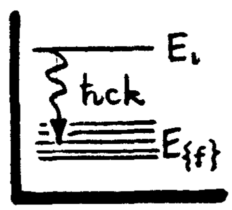
3. If there is a set of final states $\{f\}$ to which ι can decay, and the transitions are independent, the overall transition rate out of ι (for either emission or absorption processes) is the simple sum...



$$\rightarrow \Gamma_{\iota\to\{f\}} = \sum_f \Gamma_{\iota\to f} \quad \int^{\text{w/}} \begin{matrix} \text{all } f>\iota \text{ for ABSORPTION,} \\ \text{all } f<\iota \text{ for EMISSION;} \end{matrix} \Big\rangle\ \hbar ck = |E_\iota - E_f|. \tag{91}$$

For a spontaneous decay, the lifetime τ_ι of ι is: $\frac{1}{\tau_\iota} = \sum_{f<\iota} \Gamma_{\iota\to f}$.

(next page)

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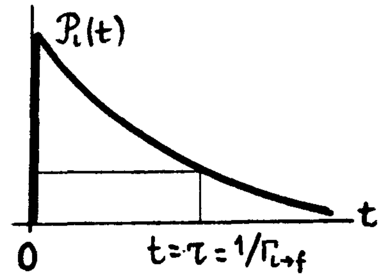
* Compared to the electric dipole rate $\Gamma \sim (Z\alpha)^4$ in Eq.(90), magnetic dipole & electric quadrupole rates are diminished by an additional factor $(Z\alpha)^2$; they are much slower.

Remarks on Γ: exponential decay law, conflict w/ $t \gg 1/\omega_{if}$.

REMARKS on Γ (cont'd)

4. The decay rate Γ of Eq. (89) is independent of time -- at least for times $t \gg 1/\omega_{if}$, per approximation in Eq. (73). Then, since Γ is the depletion rate for the probability of finding state i [when transitions $i \to f$ are possible; see Eq. (75)], we get an exponential decay law for the population $\mathcal{P}_i(t)$ of state i... viz

$$\Gamma_{i\to f}\,dt = -\frac{d\mathcal{P}_i}{\mathcal{P}_i} \Rightarrow \boxed{\mathcal{P}_i(t) = \mathcal{P}_i(0)\,e^{-\Gamma_{i\to f}t}}, \tag{92}$$



w/ $\Gamma_{i\to f} = \dfrac{4k^3}{3\hbar}|\langle f|q\mathbf{r}|i\rangle|^2$, per Eq. (89).

If i is prepared at $t=0$, it rapidly decays in a characteristic time $\tau = \dfrac{1}{\Gamma_{i\to f}}$. This is "unfortunate" for two reasons...

(A) The initial state i is depleted quickly and completely... this is not consistent with the first order time-dependent perturbation analysis we have done [beginning with Eq. (63)]. The initial state amplitude should remain $\simeq 1$, per remarks in class notes, p. tD7, on time-dependent perturbation theory.

(B) The active decay over $0 \lesssim t \sim 1/\Gamma$ may begin to conflict with the approximation $t \gg 1/\omega_{if}$ made in Eq. (73). We must certainly satisfy $1/\Gamma \gg 1/\omega_{if}$, i.e. $\omega_{if} \gg \Gamma$... in the language of Eq. (90), this requires

$$\rightarrow \omega_{if} \gg \Gamma \Rightarrow \tfrac{1}{3}\eta^2\mu^2(Z\alpha)^2\alpha \ll 1, \tag{93}$$

which is $\sim$ solidly true (for actual atoms). But at times $t \ll 1/\Gamma$ into the decay (particularly @ $t = 0+$, when decay is "tickled" into being -- see remarks on p. QF 28), we can get a conflict with $t \gg 1/\omega_{if}$.

The effort to remove the potential conflict (i.e. remove the $t \gg 1/\omega_{if}$ restriction and make the theory good @ $t = 0+$ into the decay) is quite interesting. Among other things, Γ becomes complex: $\Gamma \to \Gamma - iS$, with S interpreted as a radiative shift in the atom's energy levels. This is a subject for Weisskopf Wigner theory.