# VIIIA. APPENDIX: RADIATIVE TRANSITION RATES REVISITED

This appendix builds on the formulation presented in Review of Basic Quantum Mechanics: Dynamic Behavior of Quantum Systems, Section II of the lecture notes entitled *The Interaction of Radiation and Matter: Semiclassical Theory* (hereafter referred to as IRM:ST) to obtain explicit and reasonably general expressions for radiative transition rates. Let us suppose that a coupled system of radiation and matter is described in the Schrödinger picture by a wave function $\left|\Psi_S(t)\right\rangle$. According to Equation [ II-23 ] of IRM:ST, we may write

$$\left|\Psi_S(t)\right\rangle = \mathcal{T}_0(t)\left|\Psi_I(t)\right\rangle = \exp\left(-i\mathcal{H}_0\, t/\hbar\right)\left|\Psi_I(t)\right\rangle \qquad \text{[ VIIIA-1 ]}$$

where $\mathcal{H}_0$ is the Hamiltonian of the uncoupled radiation and matter systems. Further, Equations [ I-36a ] and [ I-37a ] of IRM:ST inform us that

$$\left|\Psi_I(t)\right\rangle = \mathcal{T}_I(t,t_0)\left|\Psi_I(t_0)\right\rangle \qquad \text{[ VIIIA-2 ]}$$

where

$$\begin{aligned} \mathcal{T}_I(t,t_0) &= 1 + \left(-\frac{i}{\hbar}\right)\int_{t_0}^{t} dt'\, \mathcal{H}_{\text{int}}^{I}(t')\,\mathcal{T}_I(t',t_0) \\ &= 1 + \left(-\frac{i}{\hbar}\right)\int_{t_0}^{t} dt'\, \mathcal{T}_0^{-1}(t')\,\mathcal{H}_{\text{int}}\,\mathcal{T}_0(t')\,\mathcal{T}_I(t',t_0) \end{aligned} \qquad \text{[ VIIIA-3 ]}$$

In IRM:ST we showed how this integral equation can be iterated to yield $\mathcal{T}_I(t,t_0)$ as a power series in $\mathcal{H}_{\text{int}}^{I}(t)$. If denote the wave functions of the uncoupled system as $\left|\psi\right\rangle$, then the probability that the coupled system is in a state $\left|\psi_f\right\rangle$ at a time $t$ is given by

$$\left|\langle\psi_f|\ \Psi_S(t)\ \rangle\right|^2 = \left|\langle\psi_f|\mathcal{T}_0(t)|\Psi_I(t)\rangle\right|^2$$
$$= \left|\langle\psi_f|\mathcal{T}_0(t)\,\mathcal{T}_I(t,t_0)\,|\Psi_I(t_0)\rangle\right|^2 \qquad \text{[ VIIIA-4 ]}$$
$$= \left|\langle\psi_f|\mathcal{T}_0(t)\,\mathcal{T}_I(t,t_0)\,\mathcal{T}_0^{-1}(t_0)\,|\Psi_S(t_0)\rangle\right|^2$$

To be more specific, if the system happened to be in state $|\psi_i\rangle$ at a time $t_0$, the probability that the coupled system is in a state $|\psi_f\rangle$ at a time $t$ is given by

$$P_{i\to f}(t,t_0) = \left|\langle\psi_f|\mathcal{T}_0(t)\,\mathcal{T}_I(t,t_0)\,\mathcal{T}_0^{-1}(t_0)\,|\psi_i\rangle\right|^2 \qquad \text{[ VIIIA-5 ]}$$

In the most experimental circumstances, we are interested in the rate at which transitions take place from some particular initial state $|\psi_i\rangle$ to a set of final states $|\psi_f\rangle$ -- *i.e.*

$$\frac{1}{\tau} \equiv \frac{d}{d\,t}\sum_f P_{i\to f}(t,t_0) = \frac{d}{dt}\sum_f \left|\langle\psi_f|\mathcal{T}_0(t)\,\mathcal{T}_I(t,t_0)\,\mathcal{T}_0^{-1}(t_0)\,|\psi_i\rangle\right|^2 \qquad \text{[ VIIIA-6 ]}$$

**<u>The first order approximation</u>** ( for $1/\tau$ ):

Using the second term in the iteration set forth in Equation [ II-27c ] of IRM:ST, we can write

$$P^{(1)}_{i\to f}(t,t_0) = \lim_{\varepsilon\to 0}\left|\langle\psi_f|\mathcal{T}_0(t)\left\{\left(-\frac{i}{\hbar}\right)\int_{-\infty}^{t} dt'\,\mathcal{T}_0^{-1}(t')\,\exp(\varepsilon\,t')\,\mathcal{H}_{\text{int}}\,\mathcal{T}_0(t')\right\}\mathcal{T}_0^{-1}(0)\,|\psi_i\rangle\right|^2$$
$$= \lim_{\varepsilon\to 0}\left|\left(-\frac{i}{\hbar}\right)\exp(-i\,\omega_f\,t)\,\langle\psi_f|\,\mathcal{H}_{\text{int}}\,|\psi_i\rangle\int_{-\infty}^{t} dt'\,\exp\left\{\left[i\,(\omega_f-\omega_i)+\varepsilon\right]\,t'\right\}\right|^2 \qquad \text{[ VIIIA-7 ]}$$
$$= \lim_{\varepsilon\to 0}\left|\frac{\langle\psi_f|\,\mathcal{H}_{\text{int}}\,|\psi_i\rangle}{\hbar}\ \frac{\exp(\varepsilon\,t-i\,\omega_i\,t)}{(\omega_i-\omega_f+i\,\varepsilon)}\right|^2$$

where the factor $\exp(\varepsilon\, t)$ was introduced to avoid the transient effects which might otherwise result from an apparent sudden application of the interaction between systems. Therefore, the first order approximation for $1/\tau$ is given by

$$\frac{1}{\tau^{(1)}} \equiv \frac{d}{d\,t}\sum_f P^{(1)}_{i\to f}(t,t_0) = \lim_{\varepsilon\to 0}\frac{d}{d\,t}\sum_f \left|\frac{\langle\psi_f|\,\mathcal{H}_{\text{int}}\,|\psi_i\rangle}{\hbar}\right|^2 \frac{\exp(2\varepsilon\, t)}{(\omega_i-\omega_f)^2+\varepsilon^2}$$

$$= \lim_{\varepsilon\to 0}\frac{2}{\hbar^2}\sum_f \left|\langle\psi_f|\,\mathcal{H}_{\text{int}}\,|\psi_i\rangle\right|^2 \frac{\varepsilon\exp(2\varepsilon\, t)}{(\omega_i-\omega_f)^2+\varepsilon^2} \qquad [\text{ VIIIA-8 }]$$

$$= \frac{2\pi}{\hbar^2}\sum_f \left|\langle\psi_f|\,\mathcal{H}_{\text{int}}\,|\psi_i\rangle\right|^2 \delta(\omega_i-\omega_f)$$

which is, of course, the generalized form of the **Fermi golden rule**.

**The second order approximation** ( for $1/\tau$ ):

Using the third term in the iteration set forth in Equation [ I-27c ] of IRM:ST, we can write

$$P^{(2)}_{i\to f}(t,t_0) = \lim_{\varepsilon\to 0}\left|\left(\frac{1}{\hbar}\right)\langle\psi_f|\,\mathcal{H}_{\text{int}}\,|\psi_i\rangle\frac{\exp(\varepsilon\, t - i\,\omega_i\, t)}{(\omega_i-\omega_f+i\,\varepsilon)}\right.$$

$$+\langle\psi_f|\mathcal{T}_0(t)\left\{\left(-\frac{i}{\hbar}\right)^2\int_{-\infty}^{t} dt'\exp(\varepsilon\, t')\,\mathcal{H}^{I}_{\text{int}}(t') \qquad [\text{ VIIIA-9a }]\right.$$

$$\left.\left.\times\int_{-\infty}^{t'} dt''\exp(\varepsilon\, t'')\,\mathcal{H}^{I}_{1\text{int}}(t'')\right\}\mathcal{T}_0^{-1}(0)\,|\psi_i\rangle\right|^2$$

or in the Schrödinger picture

$$P^{(2)}_{i\to f}(t,t_0) = \lim_{\varepsilon\to 0}\Bigg|\left(\frac{1}{\hbar}\right)\langle\psi_f|\,\mathcal{H}_{\text{int}}\,|\psi_i\rangle\,\frac{\exp(\varepsilon\, t - i\,\omega_i\, t)}{(\omega_i-\omega_f+i\,\varepsilon)}$$

$$+\langle\psi_f|\mathcal{T}_0(t)\left\{\left(-\frac{i}{\hbar}\right)^2\int_{-\infty}^{t}dt'\,\mathcal{T}_0^{-1}(t')\exp(\varepsilon\, t')\,\mathcal{H}_{\text{int}}\,\mathcal{T}_0(t')\right. \qquad \text{[ VIIIA-9b ]}$$

$$\left.\times\int_{-\infty}^{t'}dt''\,\mathcal{T}_0^{-1}(t'')\exp(\varepsilon\, t'')\,\mathcal{H}_{\text{int}}\,\mathcal{T}_0(t'')\right\}\mathcal{T}_0^{-1}(0)|\psi_i\rangle\Bigg|^2$$

Using the closure theorem we see that

$$P^{(2)}_{i\to f}(t,t_0) = \lim_{\varepsilon\to 0}\Bigg|\left(\frac{1}{\hbar}\right)\langle\psi_f|\,\mathcal{H}_{\text{int}}\,|\psi_i\rangle\,\frac{\exp(\varepsilon\, t - i\,\omega_i\, t)}{(\omega_i-\omega_f+i\,\varepsilon)}$$

$$+\left(-\frac{i}{\hbar}\right)^2\sum_m \exp(-i\,\omega_f\, t)\,\langle\psi_f|\,\mathcal{H}_{\text{int}}\,|\psi_m\rangle\langle\psi_m|\,\mathcal{H}_{\text{int}}\,|\psi_i\rangle \qquad \text{[ VIIIA-10 ]}$$

$$\times\int_{-\infty}^{t}dt'\int_{-\infty}^{t'}dt''\,\exp\left[i\,\omega_f\, t'+\varepsilon\, t'-i\,\omega_m\,(t'-t'')+\varepsilon\, t''-i\,\omega_i\, t''\right]\Bigg|^2$$

Integrating and writing the matrix elements in more concise notation, we see that

$$P^{(2)}_{i\to f}(t,t_0) = \lim_{\varepsilon\to 0}\left|\frac{\exp(\varepsilon\, t - i\,\omega_i\, t)}{(\omega_i-\omega_f+i\,\varepsilon)}\left\{\left(\frac{1}{\hbar}\right)\langle f|\,\mathcal{H}_{\text{int}}\,|i\rangle\right.\right. \qquad \text{[ VIIIA-11 ]}$$

$$\left.\left.+\left(\frac{1}{\hbar}\right)^2\sum_m\frac{\langle f|\,\mathcal{H}_{\text{int}}\,|m\rangle\langle m|\,\mathcal{H}_{\text{int}}\,|i\rangle}{\omega_i-\omega_m+i\,\varepsilon/2}\right\}\right|^2$$

Therefore, following the arguments presented above, we see that the second order approximation for $1/\tau$ is given by

$$\frac{1}{\tau^{(2)}} \equiv \frac{d}{d\,t}\sum_f P^{(2)}_{i\to f}(t,t_0)$$
$$= \frac{2\pi}{\hbar^2}\sum_f \left| \langle f|\mathcal{H}_{\text{int}}|i\rangle + \frac{1}{\hbar}\sum_m \frac{\langle f|\mathcal{H}_{\text{int}}|m\rangle\langle m|\mathcal{H}_{\text{int}}|i\rangle}{\omega_i-\omega_m}\right|^2 \delta(\omega_i-\omega_f) \qquad \text{[ VIIIA-12 ]}$$

**The nth order approximation** ( for $1/\tau$ ):

We then may make the obvious extrapolation of these results and write the nth order approximation for $1/\tau$ as

$$\frac{1}{\tau^{(n)}} = \frac{2\pi}{\hbar^2}\sum_f \left| \langle f|\mathcal{H}_{\text{int}}|i\rangle + \frac{1}{\hbar}\sum_{m_1} \frac{\langle f|\mathcal{H}_{\text{int}}|m_1\rangle\langle m_1|\mathcal{H}_{\text{int}}|i\rangle}{\omega_i-\omega_{m_1}} + \dots \right.$$
$$\left. + \left(\frac{1}{\hbar}\right)^{n-1}\sum_{m_1}\sum_{m_2}\dots\sum_{m_{n-1}} \frac{\langle f|\mathcal{H}_{\text{int}}|m_1\rangle\langle m_1|\mathcal{H}_{\text{int}}|m_2\rangle\dots\langle m_{n-1}|\mathcal{H}_{\text{int}}|i\rangle}{(\omega_i-\omega_{m_1})(\omega_i-\omega_{m_2})\dots(\omega_i-\omega_{m_{n-1}})}\right|^2 \delta(\omega_i-\omega_f) \qquad \text{[ VIIIA-13 ]}$$

where $|m_1\rangle$, $|m_2\rangle$, *etc.* could be real imtermediate states or so called ***virtual intermediate states*** for the transitions to the state $|f\rangle$. The conservation of energy holds only between $|i\rangle$ and $|f\rangle$.