Time-Dependent (Nonstationary) Perturbation Theory

Consider the Hamiltonian $\widehat{H}_0$ affected by a weak *time-dependent* perturbation $\widehat{H}_1(t)$:

$$\widehat{H} = \widehat{H}_0 + \lambda \widehat{H}_1(t).$$

(The weakness of $\widehat{H}_1$ is such that $|\langle k^{(0)}|\widehat{H}_1(t)|n^{(0)}\rangle| \ll |E_n^{(0)} - E_k^{(0)}|$.) As usual, the eigenstates $|n^{(0)}\rangle$ and eigenvalues $E_n^{(0)}$ of $\widehat{H}_0$ are known, λ is the perturbative parameter, with values from 0 ($\widehat{H} = \widehat{H}_0$) to 1 ($\widehat{H} = \widehat{H}_0 + \widehat{H}_1$). The question we ask now is, if the system is initially (e.g. $t_0 = 0$ or $-\infty$) in unperturbed state $|i^{(0)}\rangle$, will it stay in the same state at $t > 0$? Equivalently, what is the probability that it transitions to a different unperturbed state $|f^{(0)}\rangle$?

- ***Known*** The EVP of unperturbed Hamiltonian,

$$\widehat{H}_0|n^{(0)}\rangle = E_n^{(0)}|n^{(0)}\rangle, \tag{1}$$

subject to the initial condition

$$|\psi_i\rangle \equiv |\psi(0)\rangle = \sum_n a_n \, |n^{(0)}\rangle. \tag{2}$$

In these conditions, since $\widehat{H}_0$ is independent of time, the system evolves simply through the time-evolution operator $\widehat{\mathbb{U}}(t) = \exp\left(-i\widehat{H}_0 t/\hbar\right)$, that is

$$\begin{aligned} |\psi(t)\rangle = \widehat{\mathbb{U}}(t)\,|\psi_0\rangle &= \exp\left(-i\widehat{H}_0 t/\hbar\right)\sum_n a_n\,|n^{(0)}\rangle \\ &= \sum_n \underbrace{a_n \exp\left(-iE_n^{(0)} t/\hbar\right)}_{\equiv\, b_n^{(0)}(t)}\,|n^{(0)}\rangle \equiv \sum_n b_n^{(0)}(t)\,|n^{(0)}\rangle. \end{aligned} \tag{3}$$

The coefficients $b_n^{(0)}(t) = a_n \exp\left(-iE_n^{(0)} t/\hbar\right) \equiv a_n \exp(-i\omega_n t)$ (where $\omega_n = E_n^{(0)}/\hbar$) represent the zeroth-order i.e. unperturbed time evolution; they have an *implicit* time-dependence through the unitary operator, as the solution of the associated TISE.

- ***Goal*** Find the state of the system at $t > 0$ under the influence of the time-dependent Hamiltonian i.e.

$$|\psi(t)\rangle = \sum_n b_n(t)|n^{(0)}\rangle, \tag{4}$$

whose *explicitly* time-dependent coefficients $b_n(t)$ are to be determined. If the perturbation is off ($\widehat{H}_1(t) = 0$), the system evolution is governed solely by $\widehat{H}_0$. When the perturbation is on ($\widehat{H}_1(t) \neq 0$), we introduce the time-dependent coefficients $c_n(t)$ such that

$$|\psi(t)\rangle = \sum_n c_n(t) \exp\left(-iE_n^{(0)}t/\hbar\right)|n^{(0)}\rangle \equiv \sum_n c_n(t) \exp(-i\omega_n t)\,|n^{(0)}\rangle \tag{5}$$

or equivalently,

$$b_n(t) = c_n(t) \exp\left(-iE_n^{(0)}t/\hbar\right) \equiv c_n(t) \exp(-i\omega_n t), \tag{6}$$

will be determined by perturbations.

- **Note**: At this point we could insert Eq. 5 in the TDSE i.e. $\widehat{H}|\psi(t)\rangle = i\hbar\frac{d}{dt}|\psi(t)\rangle$, project it onto another unperturbed state $m^{(0)}$ i.e. scalar-multiply by $\langle m^{(0)}|$, to obtain

$$\begin{aligned} \dot{c}_m(t) &= -\frac{i}{\hbar}\sum_n c_n(t) e^{i(E_m^{(0)}-E_n^{(0)})\,t/\hbar}\,\langle m^{(0)}|\lambda\widehat{H}_1(t)|n^{(0)}\rangle \\ &\equiv -\frac{i}{\hbar}\sum_n c_n(t) e^{i(\omega_m-\omega_n)t}\,\langle m^{(0)}|\lambda\widehat{H}_1(t)|n^{(0)}\rangle, \end{aligned} \tag{7}$$

subject to initial condition (Eq. 2) $c_m(0) = b_m(0) = a_m$. While it is usually hard to solve, Eq. 7 is conceptually useful: for example, its most salient feature is the braket on the right, which indicates the <u>*transition* from state n to state m</u> (of the unperturbed system).

- **Seek**:

$$c_n(t) \stackrel{!}{=} \sum_{j=0}^{\infty} \lambda^j\, c_n^{(j)}(t) = a_n + \sum_{j=1}^{\infty} \lambda^j\, c_n^{(j)}(t), \tag{8}$$

where the second expression expresses the initial condition i.e.

$$c_n^{(0)}(t) = c_n(0) = b_n(0) = a_n. \tag{9}$$

Inserting Eq. 8 in 7, one obtains a set of first-order ODEs that couple successive perturbation orders:

$$\begin{aligned} \sum_{j=0}^{\infty} \lambda^j\, \frac{d\,c_m^{(j)}(t)}{dt} &= -\frac{i}{\hbar}\sum_{j=0}^{\infty}\sum_n \lambda^j\, c_n^{(j)}(t)\, e^{i(\omega_m-\omega_n)t}\,\langle m^{(0)}|\lambda\widehat{H}_1(t)|n^{(0)}\rangle \\ &= -\frac{i}{\hbar}\sum_{j=0}^{\infty}\sum_n \lambda^{j+1}\, c_n^{(j)}(t)\, e^{i(\omega_m-\omega_n)t}\,\langle m^{(0)}|\widehat{H}_1(t)|n^{(0)}\rangle. \end{aligned} \tag{10}$$

Next, we identify powers of λ on either side of Eq. 10 to obtain the state corrections to the desired order j:

$\boxed{\lambda^0}$

$$\frac{d\, c_m^{(0)}(t)}{d\, t} = 0 \Rightarrow c_m^{(0)}(t) = a_m = \text{const}, \tag{11}$$

$\boxed{\lambda^1}$

$$\frac{d\, c_m^{(1)}(t)}{d\, t} = -\frac{i}{\hbar} \sum_n c_n^{(0)}(t)\, e^{i\omega_{mn} t} \, \langle H_1(t) \rangle_{mn}\,, \tag{12}$$

$\boxed{\lambda^2}$

$$\frac{d\, c_m^{(2)}(t)}{d\, t} = -\frac{i}{\hbar} \sum_n c_n^{(1)}(t)\, e^{i\omega_{mn} t} \, \langle H_1(t) \rangle_{mn}\,, \text{ and so on.} \tag{13}$$

Here, $\omega_{mn} \equiv \omega_m - \omega_n$ defines the $n \to m$ transition frequency. The coefficients $c_m(t)$ of Eq. 8 are obtained to $\mathcal{O}(\lambda^2)$ by integrating Eqs. 11-13 as follows:

$$\begin{aligned} c_m(t) &= a_m - \lambda \frac{i}{\hbar} \sum_k a_k \int_0^t dt'\, e^{i\omega_{mk} t'} \, \langle H_1(t') \rangle_{mk} \\ &+ \lambda^2 \left(-\frac{i}{\hbar}\right)^2 \sum_k \sum_p a_p \int_0^t dt' \int_0^{t'} dt''\, e^{i\omega_{mk} t'}\, e^{i\omega_{kp} t''} \, \langle H_1(t') \rangle_{mk} \langle H_1(t'') \rangle_{kp} + \mathcal{O}(\lambda^3). \end{aligned} \tag{14}$$

According to Eq. 6, the coefficients $b_m(t)$ needed for the perturbed state $|\psi(t)\rangle$ of Eq. 4 are obtained simply by multiplying Eq. 14 by $\exp(-i\omega_n t)$. (**Note:** the resulting expression can also be obtained using the Interaction Picture of quantum mechanics e.g. Eq. 18.3.27 in Shankar (with $t_0 = 0$), 14.119 in Townsend etc.)

<u>In what follows, I use the subscript f for final states i.e. change m to f.</u> Thus the coefficients in Eq. 14 become $c_f(t) = a_f + c_f^{(1)}(t) + c_f^{(2)}(t) + \ldots$.

The probability that at time t, the system transitions to final state $|\psi_f^{(0)}\rangle$ (which can be one particular unperturbed state or a superposition of unperturbed states) is

$$\mathcal{P}_{fi}(t) = |\langle \psi_f^{(0)} | \psi(t) \rangle|^2.$$

- **Final state is a superposition of unperturbed states i.e.** $|\boldsymbol{\psi_f^{(0)}}\rangle = \sum_n \boldsymbol{g_n} |\boldsymbol{n^{(0)}}\rangle$ **:**

$$\mathcal{P}_{fi}(t) = \left|\sum_n g_n^* \, b_n(t)\right|^2 = \left|\sum_n g_n^* \, c_n(t) \, e^{-i\,\omega_n t}\right|^2 .$$

- **Final state is unperturbed state** $\boldsymbol{f}$ **i.e.** $|\boldsymbol{\psi_f^{(0)}}\rangle = |\boldsymbol{f^{(0)}}\rangle$ **:**

$$\begin{aligned}\mathcal{P}_{fi}(t) &= |\langle f^{(0)}|\psi(t)\rangle|^2 = |b_f(t)|^2 = |c_f(t)|^2 \\ &= |a_f + c_f^{(1)}(t) + c_f^{(2)}(t) + ...|^2\end{aligned} \tag{15}$$

Furthermore, if the initial state is unperturbed state i i.e. $|\psi_i\rangle = |i^{(0)}\rangle$, we have, from Eq. 2

$$|\psi_i\rangle = |i^{(0)}\rangle = \sum_m \delta_{mi} |m^{(0)}\rangle \Rightarrow a_m = \delta_{mi} = c_m(0) = c_m^{(0)}(t).$$

Consequently, Eq. 14 becomes, setting $\lambda = 1$,

$$\begin{aligned}c_f(t) &= \delta_{fi} + c_f^{(1)}(t) + c_f^{(2)}(t) + ... \\ &= \delta_{fi} - \frac{i}{\hbar}\int_0^t dt' \, e^{i\,\omega_{fi} t'} \, \langle H_1(t')\rangle_{fi} + \left(\frac{-i}{\hbar}\right)^2 \int_0^t dt' \int_0^{t'} dt'' \, e^{i\,\omega_{fk} t'} \, e^{i\,\omega_{ki} t''} \, \langle H_1(t')\rangle_{fk} \, \langle H_1(t'')\rangle_{ki} + ...\end{aligned} \tag{16}$$

and the $i \to f$ transition probability $\mathcal{P}_{fi}(t) = |c_f(t)|^2 = |c_f^{(1)}(t) + c_f^{(2)}(t) + ...|^2$.

Applications

Here we calculate the transition probabilities for a few simple perturbing potentials, to first-order.

1. Constant perturbation

If $\widehat{H}_1 = \widehat{V} =$ constant, then

$$\mathcal{P}_{fi}(t) = |c_f^{(1)}(t)|^2 = \left|\frac{-i}{\hbar}\int_0^t dt' \, e^{i\,\omega_{fi} t'} \, V_{fi}\right|^2$$

$$= \frac{1}{\hbar^2} |V_{fi}|^2 \left|\int_0^t dt' \, e^{i\,\omega_{fi} t'}\right|^2 = 4 \, \frac{|V_{fi}|^2}{\hbar^2 \, \omega_{fi}^2} \, \sin^2\left(\frac{\omega_{fi} \, t}{2}\right) \tag{17}$$

$$= \frac{|V_{fi}|^2}{\hbar^2} \, \pi \, t \left[\frac{\sin^2(\omega_{fi} \, t/2)}{\pi \, t \, (\omega_{fi}/2)^2}\right]$$

with $V_{fi} = \langle\psi_f|\widehat{V}|\psi_i\rangle$ and $\omega_{fi} = (E_f^{(0)} - E_i^{(0)})/\hbar$. In the long-time limit ($t \gg \omega_{fi}^{-1}$ i.e. long enough after the transition has occurred), the bracketed factor on the last line of Eq. 17 reduces to a Dirac-delta function (using Eqs. A.2 and A.4) as follows:

$$\mathcal{P}_{fi}(t) \overset{t\to\infty}{\longrightarrow} \pi\, t\, \frac{|V_{fi}|^2}{\hbar^2}\, \delta\left(\frac{\omega_{fi}}{2}\right) = \pi\, t\, \frac{|V_{fi}|^2}{\hbar^2}\, \delta\left(\frac{E_f^{(0)} - E_i^{(0}}{2\hbar}\right) = \frac{2\,\pi\, t}{\hbar}\, |V_{fi}|^2\; \delta(E_f^{(0)} - E_i^{(0)}). \tag{18}$$

The linear time dependence apparent in the transition probability is likely to pose problems since, if one waits enough, one is bound to obtain $\mathcal{P}_{fi} \to \infty$, which is utterly nonphysical! A rough way out is provided by introducing the *transition rate*, defined as the time derivative of the probability (more on this later):

$$\Gamma_{fi} = \frac{d\mathcal{P}_{fi}}{dt} \overset{t\to\infty}{\longrightarrow} \frac{2\,\pi}{\hbar}\, |V_{fi}|^2\; \delta(E_f^{(0)} - E_i^{(0)}). \tag{19}$$

The Dirac delta in Eq. 19 ensures energy conservation: the constant perturbation $\widehat{H}_1 = \widehat{V}$ neither takes nor gives energy to the system—for $t \to \infty$, transitions occur only between states with the same energy.

2. Perodic (harmonic) perturbation

Consider a perturbation of the kind $\widehat{H}_1(t) = \widehat{V} e^{\pm i\omega t}$ i.e. driven periodically with frequency ω. Then

$$\mathcal{P}_{fi}(t) = |c_f^{(1)}(t)|^2 = \left|\frac{-i}{\hbar}\int_0^t dt'\, e^{i\,\omega_{fi}t'}\; \langle H_1(t')\rangle_{fi}\right|^2$$

$$= \frac{1}{\hbar^2}\, |V_{fi}|^2 \left|\int_0^t dt'\, e^{i\,\omega_{fi}t'}\, e^{\pm i\omega t}\right|^2 = 4\, \frac{|V_{fi}|^2}{\hbar^2\, (\omega_{fi} \pm \omega)^2}\, \sin^2\left[\frac{(\omega_{fi} \pm \omega)\, t}{2}\right] \tag{20}$$

$$= \frac{|V_{fi}|^2}{\hbar^2}\, \pi\, t \left[\frac{\sin^2[(\omega_{fi} \pm \omega)\, t/2]}{\pi\, t\, [(\omega_{fi} \pm \omega)/2]^2}\right]$$

In the long-time approximation, the transition probability (Eq. 20) becomes

$$\mathcal{P}_{fi}(t) \overset{t\to\infty}{\longrightarrow} \frac{2\,\pi\, t}{\hbar}\, |V_{fi}|^2\; \delta(E_f^{(0)} - E_i^{(0)} \pm \hbar\omega) \tag{21}$$

and the transition rate

$$\Gamma_{fi}(t) \overset{t\to\infty}{\longrightarrow} \frac{2\,\pi}{\hbar}\, |V_{fi}|^2\; \delta(E_f^{(0)} - E_i^{(0)} \pm \hbar\omega) \tag{22}$$

Again, the Dirac delta in Eqs. 21 and 22 represents the conservation of energy before and after the transition. In this case, the final energy is $E_f^{(0)} = E_i^{(0)} \mp \hbar\omega$. The $-$ and $+$ signs denote, respectively, emission and absorption of one quantum of energy $\hbar\omega$. They correspond, respectively, to the $e^{\pm i\omega t}$ harmonic factors in $\widehat{H}_1$.

NOTES:

1. The fact that the linear time dependence of $\mathcal{P}_{fi}$ is "conveniently" eliminated when we calculate the transition rates does not solve the problem or superunitary probabilities long after the transition occurs!

2. Energy conservation (via the Dirac deltas) is only valid at $t \to \infty$.

3. Eqs. 19 and 22 are *approximate*. They are only valid if $E_f^{(0)} = E_i^{(0)}$ (for $\widehat{H}_1(t) =$ const) and $E_f^{(0)} = E_i^{(0)} \mp \hbar\omega$ (for $\widehat{H}_1(t) =$ periodic) *precisely*.

4. Eqs. 19 and 22 do not include momentum conservation.

3. Fermi's Golden Rule

Eqs. 19 and 22 are particular cases of the Fermi's Golden Rule (FGR). For a more realistic description, we have to account for the fact that the transitions are from an initial energy level to a *continuum* of final states. The latter can be described by a *density of states*

$$\rho(E_f) \equiv \frac{\text{number of final states}}{\text{energy interval}}.$$

The number of states within energy interval $[E_f, E_f + dE_f]$ is then equal to $\rho(E_f)\, dE_f$. (I am dropping the ^{0} superscripts.) The *total transition rate* W_{fi} is obtained by integrating Γ_{fi} over the final energy distribution, $W_{fi} = \int \Gamma_{fi}\, \rho(E_f)\, dE_f$. Thus, for constant perturbation we have

$$W_{fi} = \frac{2\pi}{\hbar}\, |V_{fi}|^2 \int \rho(E_f)\, \delta(E_f - E_i)\, dE_f = \frac{2\pi}{\hbar}\, |V_{fi}|^2\, \rho(E_i) \tag{23}$$

and for a harmonic perturbation,

$$W_{fi} = \frac{2\pi}{\hbar}\, |V_{fi}|^2 \int \rho(E_f)\, \delta(E_f - E_i \pm \hbar\omega)\, dE_f = \frac{2\pi}{\hbar}\, |V_{fi}|^2\, \rho(E_i \mp \hbar\omega). \tag{24}$$

Eqs. 23 and 24 are also embodiments of FGR.

A more detailed derivation

Consider a generic process by which a quantum system (e.g. an atom) absorbs and/or emits a particle. Examples are scattering (such as the photoelectric, Compton, and Brillouin effects), radiation absorption by atoms, spontaneous emission etc. For simplicity we assume a transition involving the emission or absorption of a single particle (photon, electron, proton, neutron etc.). The "barebones" transition rate Γ_{fi} from the initial state $|\phi_i\rangle$ to the final state $|\phi_f\rangle$, obtained as the long-time limit of the transition probability per unit time, is

$$\Gamma_{fi} = \lim_{t\to\infty} \frac{d\mathcal{P}_f}{dt} \approx \frac{2\pi}{\hbar} |\langle \phi_f | \widehat{H}_1 | \phi_i \rangle|^2 \, \delta(E_f - E_i \pm E), \tag{25}$$

where $E_{f(i)} \equiv E^0_{f(i)}$ are the unperturbed energies and $\pm E$ is the energy exchanged during the transition ($+E$ for emission, $-E$ for absorption). The delta function expresses energy conservation. The (somewhat vague) long-time premise means that the detection occurs *well after* the duration of the perturbation—embodied by an "evolutionary time" Δt—during which energy is not necessarily conserved, having an uncertainty $\Delta E \sim \hbar/\Delta t$. Beside the fuzzyness of the "long-time" notion, there is another, more systemic, difficulty with Eq. 25. First, the delta function signifies that the transition occurs between states of sharply defined energies: $E_f = E_i - E$ (emission) or $E_f = E_i + E$ (absorption). The finite resolution of the detectors, however, imposes a spread of the total final energy in an interval $[E, E + \delta E]$. Furthermore, the energy of the particle(s) exchanged does not specify the final state completely. We typically need to know in which direction and how fast the particles move hence their momentum range $[\boldsymbol{p}, \boldsymbol{p} + \delta\boldsymbol{p}]$. Therefore we have to update the transition rate to account for the final momentum and energy spreads. The solution is conceptually simple: integrate Eq. 25 over the momentum states i.e.

$$\Gamma_{fi} = \int \frac{2\pi}{\hbar} |V_{fi}|^2 \, \delta(E_f - E_i \pm E) \, d\boldsymbol{p},$$

where $V_{fi} \equiv \langle \phi_f | \widehat{H}_1 | \phi_i \rangle$. First, we need to find the number of states with momentum in $[\boldsymbol{p}, \boldsymbol{p} + d\boldsymbol{p}]$. As usual, we discretize the space via a cubic lattice of side L. At large distances from the perturbation, the wavefunction of the emitted or absorbed particle—of momentum $\boldsymbol{p}$ and energy E—can be approximated by a normalized plane wave,

$$\xi(\boldsymbol{r}, t) = \frac{e^{i\,(\boldsymbol{p}\cdot\boldsymbol{r} - Et)/\hbar}}{\sqrt{V}},$$

where $V = L^3$ is the volume of the "box" in which the process occurs. Applying periodic boundary conditions in the cube i.e.

$$\xi(x, y, z) = \xi(x + L, y, z) = \xi(x, y + L, z) = \xi(x, y, z + L)$$

leads to

$$e^{i\,p_x L/\hbar} = e^{i\,p_y L/\hbar} = e^{i\,p_z L/\hbar} = 1.$$

Thus the momentum components of the emitted/absorbed particle satisfy

$$p_x = n_x \frac{2\pi\hbar}{L} \qquad p_y = n_y \frac{2\pi\hbar}{L} \qquad p_z = n_z \frac{2\pi\hbar}{L},$$

where $n_i \in \mathbb{Z}$. Reverting to the continuous-space representation, the momentum interval becomes

$$\Delta\boldsymbol{p} = \Delta\boldsymbol{n} \frac{(2\pi\hbar)^3}{V} \to d\boldsymbol{p} \equiv d^3p = d^3n \frac{(2\pi\hbar)^3}{V}$$

where $\boldsymbol{n} = (n_x, n_y, n_z)$. In spherical coordinates, the momentum-space volume element is

$$d^3p = p^2 dp\, d\Omega_p \tag{26}$$

where $d\Omega_p = \sin\theta_p d\theta_p d\phi_p$ is the infinitesimal p-space solid angle, indicating the direction of detection (incidence) of the emitted (absorbed) particle. The infinitesimal transition rate, accompanied by the emission/absorption of a particle with momentum $\in [\boldsymbol{p}, \boldsymbol{p} + d\boldsymbol{p}]$ and energy $\in [E, E + dE]$ is then

$$\begin{aligned} d\Gamma_{fi} &= \frac{2\pi}{\hbar}\frac{V d^3p}{(2\pi\hbar)^3}\,|V_{fi}|^2\,\delta(E_f - E_i \pm E) \\ &= \frac{2\pi}{\hbar}\frac{V}{(2\pi\hbar)^3}\,p^2\left(\frac{dp}{dE}\right) dE\, d\Omega_p\,|V_{fi}|^2\,\delta(E_f - E_i \pm E) \\ &= \frac{2\pi}{\hbar}\rho(E)\, d\Omega_p\, dE\,|V_{fi}|^2\,\delta(E_f - E_i \pm E). \end{aligned} \tag{27}$$

Note: Eq. 27 is a phase-space volume element since it involves the product of spatial and momentum coordinates ($d^3r\, d^3p \to V\, d^3p$). In the last line, the density of states

$$\rho(E) d\Omega_p \equiv \frac{d^3n}{dE} = \frac{V}{(2\pi\hbar)^3}\,p^2\left(\frac{dp}{dE}\right) d\Omega_p$$

was introduced, denoting the number of states per unit energy. The updated transition rate is obtained finally by integrating Eq. 27 over the desired energy range and solid angle. For example, in the case of emission, one can choose between isotropic detection (i.e. particles emitted at all angles) and directed detection (i.e. over the solid angle subtended by a particular detector).

$$\Gamma_{fi} = \frac{2\pi}{\hbar}\int_{\text{det}} d\Omega_p \int dE\,\rho(E)\,|V_{fi}|^2\,\delta(E_f - E_i \pm E) \tag{28}$$

$$= \frac{2\pi}{\hbar}\int_{\text{det}} d\Omega_p \left[\rho(E)\,|V_{fi}|^2\right]_{E=\mp(E_f - E_i)}. \tag{29}$$

The factor in the brackets, obtained from the property of the delta function $\int f(x)\delta(x - x_0)dx = f(x_0)$, is evaluated at the exchange energy E specified by energy conservation. (Top signs: emission, bottom signs: absorption.)

1 Application examples

1.1 Emission/absorption of a photon

If the particle emitted or absorbed is a photon, it is useful to use the second expression of d^3p in Eq. 26, as a function of the relativistic photon energy $E = pc = \hbar kc = \hbar\omega$:

$$d^3p = p^2\left(\frac{dp}{dE}\right) dE\, d\Omega_p = \frac{p^2}{c} dE\, d\Omega_p = \frac{E^2}{c^3} dE\, d\Omega_p = \frac{(\hbar\omega)^2}{c^3} dE\, d\Omega_p$$

1.2 Emission/absorption of a free particle

A free particle has kinetic energy only

$$E = \frac{p^2}{2m}$$

hence

$$d^3p = p^2 \frac{m}{p}\, dE\, d\Omega_p = mp\, dE\, d\Omega_p = m(2mE)^{1/2}\, dE\, d\Omega_p$$

1.3 Emission/absorption of N free particles

For generality, here we consider the possible recoil of the quantum system that absorbs or emits particles. If N particles are emitted (e.g. decays of large nuclei, multi-photon de-excitations etc.) or absorbed (e.g. large atoms hit by photon or particle beams), the phase-space integration of Eq. 27 must now be done over *all* momenta while accounting for the conservation laws, yielding

$$\begin{aligned}\Gamma_{fi} &= \frac{2\pi}{\hbar} \underbrace{\int\int ... \int}_{N} \prod_{k=1}^{N} \rho(E_k)\, |V_{fi}|^2\, d\Omega_k dE_k\ \delta\left(E_f - E_i \pm \sum_{k'=1}^{N} E'_k\right)\ \delta\left(\boldsymbol{p}_f - \boldsymbol{p}_i - \sum_{k'=1}^{N} \boldsymbol{p}'_k\right) \\ &= \frac{2\pi}{\hbar} \underbrace{\int\int ... \int}_{\text{indep. momenta}}\ \prod_{k=1}^{N} \rho(E_k)\, |V_{fi}|^2\, d\Omega_k dE_k\ \delta\left(E_f - E_i \pm \sum_{k'=1}^{N} E'_k\right). \qquad (30)\end{aligned}$$

The first version of Eq. 30 shows the energy and momentum conservation explicitly while the second version points out that the number of integrals is actually equal to the *independent* momenta. For example, if an atom or nucleus decays into three particles, only two momenta are independent; the third is automatically set by the conservation law. Nevertheless, the phase-space product $\prod_k \rho(E_k)\, |V_{fi}|^2\, d\Omega_k dE_k$ must be over *all* particles. If the quantum system undegoing the transition is much heavier than the emitted/absorbed particles, its recoil is negligible i.e. $\boldsymbol{p}_f \approx \boldsymbol{p}_i$ and the momentum conservation factor becomes irrelevant.

Appendices

A Some properties of the Dirac Delta function

$$\delta(x) = \lim_{\epsilon \to 0} \frac{\sin(x/\epsilon)}{\pi\, x} \tag{A.1}$$

$$= \lim_{t \to \infty} \frac{\sin^2(x\, t)}{\pi x^2 t} \tag{A.2}$$

$$= \lim_{\epsilon \to 0} \frac{\epsilon}{\pi(x^2 + \epsilon^2)}. \tag{A.3}$$

$$\delta(a\, x) = \frac{\delta(x)}{|a|} \tag{A.4}$$