

Chapter 12

Time-dependent perturbation theory

So far, we have focused largely on the quantum mechanics of systems in which the Hamiltonian is time-independent. In such cases, the time dependence of a wavepacket can be developed through the time-evolution operator, $\hat{U} = e^{-i\hat{H}t/\hbar}$ or, when cast in terms of the eigenstates of the Hamiltonian, $\hat{H}|n\rangle = E_n|n\rangle$, as $|\psi(t)\rangle = e^{-i\hat{H}t/\hbar}|\psi(0)\rangle = \sum_n e^{-iE_n t/\hbar} c_n(0)|n\rangle$. Although this framework provides access to any closed quantum mechanical system, it does not describe interaction with an external environment such as that imposed by an external electromagnetic field. In such cases, it is more convenient to describe the induced interactions of a small isolated system, \hat{H}_0 , through a time-dependent interaction $V(t)$. Examples include the problem of magnetic resonance describing the interaction of a quantum mechanical spin with an external time-dependent magnetic field, or the response of an atom to an external electromagnetic field. In the following, we will develop a formalism to treat time-dependent perturbations.

12.1 Time-dependent potentials: general formalism

Consider then the Hamiltonian $\hat{H} = \hat{H}_0 + V(t)$, where all time-dependence enters through the potential $V(t)$. In the **Schrödinger representation**, the dynamics of the system are specified by the time-dependent wavefunction, $|\psi(t)\rangle_S$ through the Schrödinger equation $i\hbar\partial_t|\psi(t)\rangle_S = \hat{H}|\psi(t)\rangle_S$. However, in many cases, and in particular with the current application, it is convenient to work in the **Interaction representation**,¹ defined by

$$|\psi(t)\rangle_I = e^{i\hat{H}_0 t/\hbar}|\psi(t)\rangle_S$$

where $|\psi(0)\rangle_I = |\psi(0)\rangle_S$. With this definition, one may show that the wavefunction obeys the equation of motion (exercise)

$$i\hbar\partial_t|\psi(t)\rangle_I = V_I(t)|\psi(t)\rangle_I \quad (12.1)$$

where $V_I(t) = e^{i\hat{H}_0 t/\hbar} V e^{-i\hat{H}_0 t/\hbar}$. Then, if we form the eigenfunction expansion, $|\psi(t)\rangle_I = \sum_n c_n(t)|n\rangle$, and contract the equation of motion with a general state, $\langle n|$, we obtain

$$\boxed{i\hbar\dot{c}_m(t) = \sum_n V_{mn}(t)e^{i\omega_{mn}t}c_n(t)}, \quad (12.2)$$

¹Note how this definition differs from that of the **Heisenberg representation**, $|\psi\rangle_H = e^{i\hat{H}t/\hbar}|\psi(t)\rangle_S$ in which all time-dependence is transferred into the operators.

where the matrix elements $V_{mn}(t) = \langle m|V(t)|m\rangle$, and $\omega_{mn} = (E_m - E_n)/\hbar = -\omega_{nm}$. To develop some intuition for the action of a time-dependent potential, it is useful to consider first a periodically-driven two-level system where the dynamical equations can be solved exactly.

▷ INFO. The **two-level system** plays a special place in the modern development of quantum theory. In particular, it provides a platform to encode the simplest quantum logic gate, the **qubit**. A classical computer has a memory made up of bits, where each bit holds either a one or a zero. A quantum computer maintains a sequence of qubits. A single qubit can hold a one, a zero, or, crucially, any quantum superposition of these. Moreover, a pair of qubits can be in any quantum superposition of four states, and three qubits in any superposition of eight. In general a quantum computer with n qubits can be in an arbitrary superposition of up to 2^n different states simultaneously (this compares to a normal computer that can only be in one of these 2^n states at any one time). A quantum computer operates by manipulating those qubits with a fixed sequence of quantum logic gates. The sequence of gates to be applied is called a quantum algorithm.

An example of an implementation of qubits for a quantum computer could start with the use of particles with two spin states: $|\downarrow\rangle$ and $|\uparrow\rangle$, or $|0\rangle$ and $|1\rangle$. In fact any system possessing an observable quantity A which is conserved under time evolution and such that A has at least two discrete and sufficiently spaced consecutive eigenvalues, is a suitable candidate for implementing a qubit. This is true because any such system can be mapped onto an effective spin-1/2 system.

▷ EXAMPLE: **Dynamics of a driven two-level system:** Let us consider a two-state system with

$$\hat{H}_0 = \begin{pmatrix} E_1 & 0 \\ 0 & E_2 \end{pmatrix}, \quad V(t) = \begin{pmatrix} 0 & \delta e^{i\omega t} \\ \delta e^{-i\omega t} & 0 \end{pmatrix}.$$

Specifying the wavefunction by the two-component vector, $\mathbf{c}(t) = (c_1(t) \ c_2(t))$, Eq. (12.2) translates to the equation of motion (exercise)

$$i\hbar\partial_t\mathbf{c} = \delta \begin{pmatrix} 0 & e^{i(\omega-\omega_{21})t} \\ e^{-i(\omega-\omega_{21})t} & 0 \end{pmatrix} \mathbf{c}(t),$$

where $\omega_{21} = (E_2 - E_1)/\hbar$. With the initial condition $c_1(0) = 1$, and $c_2(0) = 0$, this equation has the solution,

$$|c_2(t)|^2 = \frac{\delta^2}{\delta^2 + \hbar^2(\omega - \omega_{21})^2/4} \sin^2 \Omega t, \quad |c_1(t)|^2 = 1 - |c_2(t)|^2,$$

where $\Omega = ((\delta/\hbar)^2 + (\omega - \omega_{21})^2/4)^{1/2}$ is known as the **Rabi frequency**. The solution, which varies periodically in time, describes the transfer of probability from state 1 to state 2 and back. The maximum probability of occupying state 2 is a Lorentzian with

$$|c_2(t)|_{\max}^2 = \frac{\gamma^2}{\gamma^2 + \hbar^2(\omega - \omega_{21})^2/4},$$

taking the value of unity at resonance, $\omega = \omega_{21}$.

▷ EXERCISE. Derive the solution from the equations of motion for $\mathbf{c}(t)$. Hint: eliminate c_1 from the equations to obtain a second order differential equation for c_2 .



▷ INFO. The dynamics of the driven two-level system finds practical application in the **Ammonia maser**: The ammonia molecule NH_3 has a pyramidal structure with an orientation characterised by the position of the “lone-pair” of electrons sited

on the nitrogen atom. At low temperature, the molecule can occupy two possible states, $|A\rangle$ and $|S\rangle$, involving symmetric (S) or an antisymmetric (A) atomic configurations, separated by a small energy splitting, ΔE . (More precisely, along the axis of three-fold rotational symmetry, the effective potential energy of the nitrogen atom takes the form of a double-well. The tunneling of the nitrogen atom through the double well leads to the symmetric and asymmetric combination of states.) In a time-dependent uniform electric field the molecules experience a potential $V = -\boldsymbol{\mu}_d \cdot \mathbf{E}$, where $\mathbf{E} = E\hat{e}_z \cos \omega t$, and $\boldsymbol{\mu}_d$ denotes the electric dipole moment. Since $\boldsymbol{\mu}_d$ is odd under parity transformation, $P\boldsymbol{\mu}_d P = -\boldsymbol{\mu}_d$, and $P|A\rangle = -|A\rangle$ and $P|S\rangle = |S\rangle$, the matrix elements of the electric dipole moment are off-diagonal: $\langle S|\boldsymbol{\mu}_d|S\rangle = \langle A|\boldsymbol{\mu}_d|A\rangle = 0$ and $\langle S|\boldsymbol{\mu}_d|A\rangle = \langle S|\boldsymbol{\mu}_d|A\rangle \neq 0$.

If we start with all of the molecules in the symmetric ground state, we have shown above that the action of an oscillating field for a particular time can drive a collection of molecules from their ground state into the antisymmetric first excited state. The ammonia maser works by sending a stream of ammonia molecules, traveling at known velocity, down a tube having an oscillating field for a definite length, so the molecules emerging at the other end are all (or almost all, depending on the precision of ingoing velocity, etc.) in the first excited state. Application of a small amount of electromagnetic radiation of the same frequency to the outgoing molecules will cause some to decay, generating intense radiation and therefore a much shorter period for all to decay, emitting coherent radiation.

Charles Hard Townes 1915- (left)

is an American Nobel prize-winning physicist and educator.



Townes is known for his work on the theory and application of the maser – microwave amplification by stimulated emission of radiation, on which he got the fundamental patent, and other work in quantum electronics connected with both maser and laser devices. He received the Nobel Prize in Physics in 1964.

12.2 Time-dependent perturbation theory

We now turn to consider a generic time-dependent Hamiltonian for which an analytical solution is unavailable – sadly the typical situation! In this case, we must turn to a perturbative analysis, looking for an expansion of the basis coefficients $c_n(t)$ in powers of the interaction,

$$c_n(t) = c_n^{(0)} + c_n^{(1)}(t) + c_n^{(2)}(t) + \dots,$$

where $c_n^{(m)} \sim O(V^m)$ and $c_n^{(0)}$ is some (time-independent) initial state. The programme to complete this series expansion is straightforward but technical.

▷ INFO. In the interaction representation, the state $|\psi(t)\rangle_I$ can be related to an initial state $|\psi(t_0)\rangle_I$ through the time-evolution operator, $U_I(t, t_0)$, i.e. $|\psi(t)\rangle_I = U_I(t, t_0)|\psi(t_0)\rangle_I$. Since this is true for any initial state $|\psi(t_0)\rangle_I$, from Eq. (12.1), we must have

$$i\hbar\partial_t U_I(t, t_0) = V_I(t)U_I(t, t_0),$$

with the boundary condition $U_I(t_0, t_0) = \mathbb{I}$. Integrating this equation from t_0 to t , formally we obtain,

$$U_I(t, t_0) = \mathbb{I} - \frac{i}{\hbar} \int_{t_0}^t dt' V_I(t') U_I(t', t_0).$$

This result provides a *self-consistent* equation for $U_I(t, t_0)$, i.e. if we take this expression and substitute $U_I(t', t_0)$ under the integrand, we obtain

$$U_I(t, t_0) = \mathbb{I} - \frac{i}{\hbar} \int_{t_0}^t dt' V_I(t') + \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^t dt' V_I(t') \int_{t_0}^{t'} dt'' V_I(t'') U_I(t'', t_0).$$

Iterating this procedure, we thus obtain

$$U_I(t, t_0) = \sum_{n=0}^{\infty} \left(-\frac{i}{\hbar}\right)^n \int_{t_0}^t dt_1 \cdots \int_{t_0}^{t_{n-1}} dt_n V_I(t_1) V_I(t_2) \cdots V_I(t_n), \quad (12.3)$$

where the term $n = 0$ translates to \mathbb{I} . Note that the operators $V_I(t)$ are organised in a time-ordered sequence, with $t_0 \leq t_n \leq t_{n-1} \leq \dots \leq t_1 \leq t$. With this understanding, we can write this expression more compactly as

$$U_I(t, t_0) = \mathbb{T} \left[e^{-\frac{i}{\hbar} \int_{t_0}^t dt' V_I(t')} \right],$$

where “ \mathbb{T} ” denotes the time-ordering operator and its action is understood by Eq. (12.3).

If a system is prepared in an initial state, $|i\rangle$ at time $t = t_0$, at a subsequent time, t , the system will be in a final state,

$$|i, t_0, t\rangle = U_I(t, t_0)|i\rangle = \sum_n |n\rangle \overbrace{\langle n|U_I(t, t_0)|i\rangle}^{c_n(t)}.$$

Making use of Eq. (12.3), and the resolution of identity, $\sum_m |m\rangle\langle m| = \mathbb{I}$, we obtain

$$c_n(t) = \delta_{ni} \overbrace{\phantom{-\frac{i}{\hbar} \int_{t_0}^t dt' \langle n|V_I(t')|i\rangle}}^{c_n^{(0)}} - \frac{i}{\hbar} \int_{t_0}^t dt' \langle n|V_I(t')|i\rangle \overbrace{\phantom{-\frac{1}{\hbar^2} \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' \sum_m \langle n|V_I(t')|m\rangle \langle m|V_I(t'')|i\rangle}}^{c_n^{(1)}} - \frac{1}{\hbar^2} \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' \sum_m \langle n|V_I(t')|m\rangle \langle m|V_I(t'')|i\rangle \overbrace{}^{c_n^{(2)}} + \dots.$$

Recalling that $V_I = e^{i\hat{H}_0 t/\hbar} V e^{-i\hat{H}_0 t/\hbar}$, we thus find that

$$\boxed{\begin{aligned} c_n^{(1)}(t) &= -\frac{i}{\hbar} \int_{t_0}^t dt' e^{i\omega_{ni}t'} V_{ni}(t') \\ c_n^{(2)}(t) &= -\frac{1}{\hbar^2} \sum_m \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' e^{i\omega_{nm}t' + i\omega_{mi}t''} V_{nm}(t') V_{mi}(t''), \end{aligned}} \quad (12.4)$$

where $V_{nm}(t) = \langle n|V(t)|m\rangle$ and $\omega_{nm} = (E_n - E_m)/\hbar$, etc. In particular, the probability of effecting a transition from state $|i\rangle$ to state $|n\rangle$ for $n \neq i$ is given by $P_{i \rightarrow n} = |c_n(t)|^2 = |c_n^{(1)}(t) + c_n^{(2)}(t) + \dots|^2$.

▷ **EXAMPLE: The kicked oscillator:** Suppose a simple harmonic oscillator is prepared in its ground state $|0\rangle$ at time $t = -\infty$. If it is perturbed by a small time-dependent potential $V(t) = -eEx e^{-t^2/\tau^2}$, what is the probability of finding it in the first excited state, $|1\rangle$, at $t = +\infty$?

Working to the first order of perturbation theory, the probability is given by $P_{0 \rightarrow 1} \simeq |c_1^{(1)}|^2$ where $c_1^{(1)}(t) = -\frac{i}{\hbar} \int_{t_0}^t dt' e^{i\omega_{10}t'} V_{10}(t')$, $V_{10}(t') = -eE\langle 1|x|0\rangle e^{-t'^2/\tau^2}$ and $\omega_{10} = \omega$. Using the ladder operator formalism, with $|1\rangle = a^\dagger|0\rangle$ and $x = \sqrt{\frac{\hbar}{2m\omega}}(a + a^\dagger)$, we have $\langle 1|x|0\rangle = \sqrt{\frac{\hbar}{2m\omega}}$. Therefore, making use of the identity $\int_{-\infty}^{\infty} dt' \exp[i\omega t' - t'^2/\tau^2] = \sqrt{\pi}\tau \exp[-\omega^2\tau^2/4]$, we obtain the transition amplitude, $c_1^{(1)}(t \rightarrow \infty) = ieE\tau \sqrt{\frac{\pi}{2m\hbar\omega}} e^{-\omega^2\tau^2/4}$. As a result, we obtain the transition probability, $P_{0 \rightarrow 1} \simeq (eE\tau)^2 (\pi/2m\hbar\omega) e^{-\omega^2\tau^2/2}$. Note that the probability is maximized for $\tau \sim 1/\omega$.

▷ **EXERCISE.** Considering the same perturbation, calculate the corresponding transition probability from the ground state to the *second* excited state. Hint: note that this calculation demands consideration of the second order of perturbation theory.

12.3 “Sudden” perturbation

To further explore the time-dependent perturbation theory, we turn now to consider the action of fast or “sudden” perturbations. Here we define sudden as a perturbation in which the switch from one time-independent Hamiltonian \hat{H}_0 to another \hat{H}'_0 takes place over a time much shorter than any natural period of the system. In this case, perturbation theory is irrelevant: if the system is initially in an eigenstate $|n\rangle$ of \hat{H}_0 , its time evolution following the switch will follow that of \hat{H}'_0 , i.e. one simply has to expand the initial state as a sum over the eigenstates of \hat{H}'_0 , $|n\rangle = \sum_{n'} |n'\rangle \langle n'|n\rangle$. The non-trivial part of the problem lies in establishing that the change is sudden enough. This is achieved by estimating the actual time taken for the Hamiltonian to change, and the periods of motion associated with the state $|n\rangle$ and with its transitions to neighboring states.

12.3.1 Harmonic perturbations: Fermi’s Golden Rule

Let us then consider a system prepared in an initial state $|i\rangle$ and perturbed by a periodic harmonic potential $V(t) = Ve^{-i\omega t}$ which is abruptly switched on at time $t = 0$. This could represent an atom perturbed by an external oscillating electric field, such as an incident light wave. What is the probability that, at some later time t , the system lies in state $|f\rangle$?

From Eq. (12.4), to first order in perturbation theory, we have

$$c_f^{(1)}(t) = -\frac{i}{\hbar} \int_0^t dt' \langle f|V|i\rangle e^{i(\omega_f - \omega)t'} = -\frac{i}{\hbar} \langle f|V|i\rangle \frac{e^{i(\omega_f - \omega)t} - 1}{i(\omega_f - \omega)}.$$

The probability of effecting the transition after a time t is therefore given by

$$P_{i \rightarrow f}(t) \simeq |c_f^{(1)}(t)|^2 = \frac{1}{\hbar^2} |\langle f|V|i\rangle|^2 \left(\frac{\sin((\omega_f - \omega)t/2)}{(\omega_f - \omega)/2} \right)^2.$$

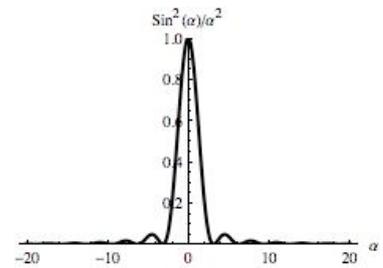
Setting $\alpha = (\omega_f - \omega)/2$, the probability takes the form $\sin^2(\alpha t)/\alpha^2$ with a peak at $\alpha = 0$, with maximum value t^2 and width of order $1/t$ giving a total weight of order t . The function has more peaks positioned at $\alpha t = (n + 1/2)\pi$. These are bounded by the denominator at $1/\alpha^2$. For large t their contribution comes from a range of order $1/t$ also, and as $t \rightarrow \infty$ the function tends towards a δ -function centred at the origin, but multiplied by t , i.e. the likelihood of transition is proportional to time elapsed. We should therefore divide by t to get the transition rate.

Finally, with the normalisation, $\int_{-\infty}^{\infty} d\alpha \left(\frac{\sin(\alpha t)}{\alpha} \right)^2 = \pi t$, we may effect the replacement, $\lim_{t \rightarrow \infty} \frac{1}{t} \left(\frac{\sin(\alpha t)}{\alpha} \right)^2 = \pi \delta(\alpha) = 2\pi \delta(2\alpha)$ leading to the following expression for the transition rate,

$$R_{i \rightarrow f}(t) = \lim_{t \rightarrow \infty} \frac{P_{i \rightarrow f}(t)}{t} = \frac{2\pi}{\hbar^2} |\langle f|V|i\rangle|^2 \delta(\omega_f - \omega). \quad (12.5)$$

This expression is known as **Fermi’s Golden Rule**.² One might worry that, in the long time limit, we found that the probability of transition is in fact

²Curiously, although named after Fermi, most of the work leading to the Golden Rule was undertaken in an earlier work by Dirac, (P. A. M. Dirac, *The quantum theory of emission and absorption of radiation*. Proc. Roy. Soc. (London) A **114**, 243265 (1927)) who formulated an almost identical equation, including the three components of a constant, the matrix element of the perturbation and an energy difference. It is given its name due to the fact that, being such a useful relation, Fermi himself called it “Golden Rule No. 2” (E. Fermi, *Nuclear Physics*, University of Chicago Press, 1950).



Plot of $\sin^2(\alpha t)/\alpha^2$ for $t = 1$. Note that, as $t \rightarrow \infty$, this function asymptotes to a δ -function, $\pi t \delta(\alpha)$.

Enrico Fermi 1901-1954:

An Italian physicist most noted for his work on the development of the first nuclear reactor, and for his contributions to the development of quantum



theory, nuclear and particle physics, and statistical mechanics. Fermi was awarded the Nobel Prize in Physics in 1938 for his work on induced radioactivity and is today regarded as one of the most influential scientists of the 20th century. He is acknowledged as a unique physicist who was highly accomplished in both theory and experiment. Fermium, a synthetic element created in 1952 is named after him.

diverging — so how can we justify the use of perturbation theory? For a transition with $\omega_{fi} \neq \omega$, the “long time” limit is reached when $t \gg 1/(\omega_{fi} - \omega)$, a value that can still be very short compared with the mean transition time, which depends on the matrix element. In fact, Fermi’s Rule agrees extremely well with experiment when applied to atomic systems.

▷ INFO. **Alternative derivation of the Golden Rule:** When light falls on an atom, the full periodic potential is not suddenly imposed on an atomic time scale, but builds up over many cycles (of the atom and of the light). If we assume that $V(t) = e^{\varepsilon t} V e^{-i\omega t}$, with ε very small, V is switched on very gradually in the past, and we are looking at times much smaller than $1/\varepsilon$. We can then take the initial time to be $-\infty$, that is,

$$c_f^{(1)}(t) = -\frac{i}{\hbar} \int_{-\infty}^t \langle f|V|i \rangle e^{i(\omega_{fn} - \omega - i\varepsilon)t'} dt' = -\frac{1}{\hbar} \frac{e^{i(\omega_{fn} - \omega - i\varepsilon)t}}{\omega_{fn} - \omega - i\varepsilon} \langle f|V|i \rangle,$$

i.e. $|c_f(t)|^2 = \frac{1}{\hbar^2} \frac{e^{2\varepsilon t}}{(\omega_{fn} - \omega)^2 + \varepsilon^2} |\langle f|V|i \rangle|^2$. Applied to the transition rate $\frac{d}{dt} |c_f^{(1)}(t)|^2$, the identity $\lim_{\varepsilon \rightarrow 0} \frac{2\varepsilon}{(\omega_{fn} - \omega)^2 + \varepsilon^2} \rightarrow 2\pi\delta(\omega_{fn} - \omega)$ leads to the Golden Rule.

From the expression for the Golden rule (12.5) we see that, for transitions to occur, and to satisfy energy conservation:

- (a) the final states must exist over a continuous energy range to match $\Delta E = \hbar\omega$ for fixed perturbation frequency ω , or
- (b) the perturbation must cover a sufficiently wide spectrum of frequency so that a discrete transition with a fixed $\Delta E = \hbar\omega$ is possible.

For two discrete states, since $|V_{fi}|^2 = |V_{if}|^2$, we have the semiclassical result $P_{i \rightarrow f} = P_{f \rightarrow i}$ — a statement of **detailed balance**.

12.3.2 INFO: Harmonic perturbations: second-order transitions

Although the first order perturbation theory is often sufficient to describe transition probabilities, sometimes first order matrix element, $\langle f|V|i \rangle$ is identically zero due to symmetry (e.g. under parity, or through some selection rule, etc.), but other matrix elements are non-zero. In such cases, the transition may be accomplished by an indirect route. We can estimate the transition probabilities by turning to the second order of perturbation theory (12.4),

$$c_f^{(2)}(t) = -\frac{1}{\hbar^2} \sum_m \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' e^{i\omega_{fm}t' + i\omega_{mi}t''} V_{fm}(t') V_{mi}(t'').$$

If, as above, we suppose that a harmonic potential perturbation is gradually switched on, $V(t) = e^{\varepsilon t} V e^{-i\omega t}$, with the initial time $t_0 \rightarrow -\infty$, we have

$$c_f^{(2)}(t) = -\frac{1}{\hbar^2} \sum_m \langle f|V|m \rangle \langle m|V|i \rangle \int_{-\infty}^t dt' \int_{-\infty}^{t'} dt'' e^{i(\omega_{fm} - \omega - i\varepsilon)t'} e^{i(\omega_{mi} - \omega - i\varepsilon)t''}.$$

The integrals are straightforward, and yield

$$c_n^{(2)} = -\frac{1}{\hbar^2} e^{i(\omega_{fn} - 2\omega)t} \frac{e^{2\varepsilon t}}{\omega_{fn} - 2\omega - 2i\varepsilon} \sum_m \frac{\langle f|V|m \rangle \langle m|V|i \rangle}{\omega_m - \omega_i - \omega - i\varepsilon}.$$

Then, following our discussion above, we obtain the transition rate:

$$\frac{d}{dt} |c_n^{(2)}|^2 = \frac{2\pi}{\hbar^4} \left| \sum_m \frac{\langle f|V|m \rangle \langle m|V|i \rangle}{\omega_m - \omega_i - \omega - i\varepsilon} \right|^2 \delta(\omega_{fn} - 2\omega).$$

This is a transition in which the system gains energy $2\hbar\omega$ from the harmonic perturbation, i.e. two “photons” are absorbed in the transition, the first taking the system to the intermediate energy ω_m , which is short-lived and therefore not well defined in energy – indeed there is no energy conservation requirement for the virtual transition into this state, only between initial and final states. Of course, if an atom in an arbitrary state is exposed to monochromatic light, other second order processes in which two photons are emitted, or one is absorbed and one emitted (in either order) are also possible.