Time Dependent Perturbation Theory

These notes give a simple description of time dependent perturbation theory, leading to a general approach for evaluation of transition rates to leading order in the strength of the perturbation. Applications to radiative transitions are discussed.

### Time dependent perturbations

#### Introduction

The basic problem is to consider a time dependent perturbation

\[ H = H_0 + V(t) \]

Sometimes \( V \) is labeled \( H_1 \) or \( H_I \). It is assumed that eigenstates and eigenvalues of the unperturbed Hamiltonian are known

\[ H_0 \ket{n} = E_n \ket{n} \]

The general time dependent state can be written as

\[ \ket{\alpha, t} = \sum_n c_n(t) e^{-i \frac{E_n}{\hbar} t} \ket{n} \]

In this notation, the time evolution of the states is shown explicitly, so the \( \ket{n} \) are defined at fixed initial time. The remaining time evolution is carried by the expansion coefficients, some of which is known from the unperturbed states, and some of which arises from the effect of \( V \). The discussion starts in the Schroedinger picture, but ends up in the interaction picture as the simple time dependence \( e^{-i \frac{E_n}{\hbar} t} \) gets shifted from the states to the operator \( V \).

A central problem of time dependent perturbation theory is then: starting from some initial state, what is the probability to find the system in eigenstate \( \ket{n} \) at some later time. Formally, this is just

\[
P_n(t) = \left| \braket{n | \alpha, t} \right|^2 = \left| \braket{n | \sum_m c_m(t) e^{-i \frac{E_m}{\hbar} t} \ket{m}} \right|^2 = \left| \sum_m c_m(t) e^{-i \frac{E_m}{\hbar} t} \delta_{nm} \right|^2 = \left| c_n(t) e^{-i \frac{E_n}{\hbar} t} \right|^2 = |c_n(t)|^2
\]

#### Solution for \( c_n(t) \) as a set of coupled differential eqs.

The time dependence of the \( c_n \) is given by

\[
i \hbar \frac{\partial}{\partial t} \ket{\alpha} = (H_0 + V(t)) \ket{\alpha}
\]

Substituting in the expansion
To simplify the discussion, take the initial condition to be such that just one state $|i\rangle$ is occupied at $t = 0$, i.e. $c_n(0) = \delta_{ni}$. Then, the leading order term in a perturbation series is given by

$$\hat{c}_n = -\frac{i}{\hbar} \langle n | V(t) | i \rangle e^{i\omega_{ni} t}$$

**Case of sudden turn on of constant $V$**

As a first example, consider the sudden turn on of an otherwise static potential. This is a problem that can be treated in time independent perturbation theory - so it makes a good contact point for discussing the time dependent theory. The potential is given by
\[ V(t) = 0 \text{, } t < 0 \]
\[ = V_{nu}, \text{ } t > 0 \]

where the \( V_{nu} \) are just constants. Then the solution to the differential equation is

\[
c_n(t) = -\frac{1}{\hbar} \int_0^t \langle n | V | i \rangle e^{i \omega_n t} dt
\]
\[
= -\frac{\langle n | V | i \rangle}{\hbar \omega_n} \left[ e^{i \omega_n t} \right]_0^t \]
\[
= \frac{\langle n | V | i \rangle}{\hbar \omega_n} \left( 1 - e^{i \omega_n t} \right)
\]
\[
= \frac{\langle n | V | i \rangle}{E_n - E_i} \left( 1 - e^{i \omega_n t} \right)
\]

The probability to be found in the state \(| n \rangle\) is then

\[
P_n = |c_n|^2
\]
\[
= \frac{|\langle n | V | i \rangle|^2}{\hbar^2 \omega_n^2} \left( 1 - \cos \omega_n t \right)
\]
\[
= \frac{4|\langle n | V | i \rangle|^2}{\hbar^2 \omega_n^2} \sin^2 \left( \frac{\omega_n t}{2} \right)
\]

**Connections**

The result for \( P_n \) has several interpretations …

**a) to time independent perturbation theory**

As stated above, these results are compatible with time independent perturbation theory. Specifically, in that approach, one would solve for the new eigenstates \(| n' \rangle\) after the perturbation is turned on. Since the perturbation is turned on suddenly, the system originally in state \(| i \rangle\) finds itself in the new states \(| n \rangle\) with an amplitude \( c_n^1 = \frac{\langle n | V | i \rangle}{E_n - E_i} \). Since the states are not degenerate, the energy splitting provides for the state to evolve in a non-trivial manner - i.e. we subtract out the common phase inherent in the initial state. At first the probability to be in any state other than the initial one is zero, but after some time the small piece of the system in one of the other eigenstates is out of phase with the original state. At this point there is some non-zero probability for the system to be found in states of the unperturbed basis other than the original state \(| i \rangle\).

**b) interpretation of \( \sin^2 \left( \frac{\omega t}{\omega^2} \right) \)**

In the limit of large time \( \frac{\sin^2 \left( \frac{\omega t}{\omega^2} \right)}{\omega^2} \) is sharply peaked at \( \omega = 0 \). The height of the function is \( t^2 \), whereas the width is \( \frac{1}{t} \). Here is a plot for \( t = 10 \).
The total area increases with $t$, but because the function gets narrower, it approximates a delta function.

$$\frac{\sin^2(\omega t)}{\omega^2} \to \pi t \delta(\omega)$$

The interpretation given to this $\delta$-function is that it enforces energy conservation. If one considers shorter times, the width of the $\sin(\omega t)$ function is compatible with the uncertainty principle $\delta t \delta E \sim h$.

**c) Transition rates and Fermi’s golden rule**

This interpretation is appropriate when there is a continuum of final states. For example, a typical calculation is to find the total transition probability to all states after some time.

$$P_{\text{tot}} = \sum_n P_{i \rightarrow n} = \int d\omega P_{i \rightarrow n}$$

$$= \int d\omega \frac{4|\langle \omega \rangle|^2}{\hbar^2 \omega_n^2} \sin^2 \left( \frac{\omega_n t}{2} \right)$$

$$= \int d\omega \frac{2\pi}{\hbar^2} |V_{ni}|^2 \delta(\omega_n) t$$

where $V_{ni} = \langle n \mid V \mid i \rangle$. Dividing both sides by $t$, one finds the transition rate

$$\Gamma = \frac{P}{t} = \int d\omega \frac{2\pi}{\hbar^2} |V_{ni}|^2 \delta(\omega_n)$$

The integral over states is typically recast in terms of an integral over final state energy convoluted with an energy dependent density of states, which is determined from phase space considerations.

$$\int d\omega = \int \frac{dn}{dE} dE = \int \rho(E_f) dE_f$$

The final result is Fermi’s Golden Rule,

$$\Gamma = \frac{P}{t} = \int \frac{2\pi}{\hbar^2} |V_{fi}|^2 \delta(\omega_f) \rho(E_f) dE_f$$

$$= \frac{2\pi}{\hbar^2} |V_{fi}|^2 \rho(E_f)$$
d) $V(t) = \Theta(t) e^{i\omega t}$, emission, absorption and detailed balance

The next example is to consider the oscillatory perturbation $V(t) = V_{mn} e^{i\omega t}$. This results in a similar formula except the frequency is shifted $\omega_{mn} \rightarrow \omega_{mn} \pm \omega$, or the final state energy is shifted by $E_f = E_i + \hbar \omega$. The system absorbs energy from the perturbing force, in units of $\omega$.

Similarly, if one considers the harmonic form $\cos(\omega t) = \frac{1}{2} (e^{i\omega t} + e^{-i\omega t})$ then one can have energy emission as well, where the system loses energy to the perturbation force. Thus, there is a unified model for absorption and emission of energy. Note that the two terms have essentially the same matrix element. Indeed, since the square of the forward and back matrix elements are the same, the rate at which a system prepared in state $i$ absorbs energy will be equal to the rate at which a system prepared in state $f$ emits energy - except for considerations of the density of states and how those states are occupied. Qualitatively

$$\frac{\Gamma_{\omega t}}{\Gamma_{\omega t}} = \frac{2n}{\hbar^2} \frac{|V_{ir}|^2 \rho(E_i)}{|V_{jr}|^2 \rho(E_r)} = \frac{\rho(E_f)}{\rho(E_i)}$$

This is the starting point for a discussion of the principle of detailed balance in a statistical treatment of reaction rate equations. A full treatment includes statistical mechanics factors for occupation of the initial and final states.

e) Full solution for 2 state problem

Sakurai considers the full solution for the two state problem,

$$H = \begin{pmatrix} E_1 & \gamma e^{i\omega t} \\ \gamma^* e^{-i\omega t} & E_2 \end{pmatrix}$$

For the initial condition $c_1(0) = 1, c_2(0) = 0$, the probability for the system to be found in state $|2\rangle$ after some time is

$$P_2 = |c_2(t)|^2 = \frac{4\gamma^2}{\hbar^2} \frac{1}{11^2} \sin^2[\Omega t] \quad \text{with} \quad \Omega = \left(\frac{4\gamma^2}{\hbar^2} + (\omega - \omega_2)^2\right)^{1/2}.$$ 

A few comments are in order. First, apart from the change of $(\omega - \omega_2) \rightarrow \Omega$, the formula is the same as given for $P_n$ above. For the two state system, if $\gamma$ is "small" one may think of the solution for $P_n$ as an approximation to $P_2$. Note, however, that $\Omega$ never goes to zero, so there is no $\delta(\omega)$. Even so, if $\gamma$ is very small, $P_2$ is sharply peaked at $\omega = \omega_2$. Also, the deviation from the leading behavior, depends not on the frequency, but on the strength of the perturbation. There are two "energy scales" in the problem, $\gamma$ and $\hbar \omega$.

Radiative transitions

A framework has been established which treats time dependent perturbations as a means for driving transitions between states of a system. The rate of transitions is proportional to the square of the transition matrix element. Energy conservation is explicitly realised by $\delta(E_f - E_i \pm \hbar \omega)$, i.e. the energy transfer between the system and the external perturbation is constrained to units of energy equal to the driving frequency of the perturbation.
Depending on the initial and final states, the transition is interpreted as absorption of a photon, spontaneous or stimulated emission of a photon, a transition between bound states in an external potential, photo-ionization of an atom, etc. In order to provide these different interpretations it is useful to quantize the electromagnetic field, producing a Fock space for photons. It is also necessary to present concepts of phase space, and the geometry of scattering. A brief discussion of the Born approximation for scattering of a particle beam by a target, is given at the end.

### The electron-radiation interaction Hamiltonian

The interaction Hamiltonian involves the vector potential $\vec{A}$, which can be treated classically, or as a quantized field with states specified by their Fock space representation.

Specifically, the evolution of a hydrogenic atom in an oscillating electromagnetic field is described by the Hamiltonian

$$H = \frac{(p - e A)^2}{2m} + e \phi = \frac{p^2}{2m} + e \phi - \frac{e}{2mc^2} (p \cdot A) + \frac{e^2}{2mc^2} A^2 = \frac{p^2}{2m} + e \phi - \frac{e}{m} A \cdot p + \frac{e^2}{2mc^2} A^2 \\ \approx \frac{p^2}{2m} + e \phi - \frac{e}{m} A \cdot p$$

where in going from line 2→3, one works in the "Coulomb" gauge where $\nabla \cdot A = 0$ or $[p, A] = 0$, and in the last line we have dropped the $A^2$ term since it is higher order in the charge $e$, that is we are treating $e$ as the parameter which describes the strength of the perturbation. If one developed the full perturbation series (not done in these notes) and then worked to higher than first order, then it would be necessary to retain the $A^2$ term in the analysis.

The full Hamiltonian is then a combination of a known problem $H_0 = \frac{p^2}{2m} + e \phi$, and a perturbation $H_1(t) = -\frac{e}{mc} A \cdot p$. For atomic transitions, the unperturbed basis states are the bound states of the hydrogen atom.

### Vector potential for classical plane waves

The vector potential for a linearly polarized electromagnetic wave can be written as

$$\vec{A} = 2 A_0 \vec{\epsilon} \cos(\vec{k} \cdot \vec{x} - \omega t) = A_0 \vec{\epsilon} (e^{i(kx-\omega t)} + e^{-i(kx-\omega t)})$$

where $A_0$ gives the strength of the field, $\vec{\epsilon}$ is the polarization tensor, $\vec{k}$ is the wave vector for the field and $\omega$ is the frequency. For light, $\omega = k c$. This formalism is valid for electromagnetic radiation, but a similar formalism could be developed for interactions with other wave fields, for example phonons. Continuing, the perturbation is

$$H_1(t) = -\frac{e}{mc} A \cdot p = -\frac{e}{mc} A_0 (\vec{\epsilon} \cdot p) (e^{i(kx-\omega t)} + e^{-i(kx-\omega t)}) = V e^{i\omega t} + V^* e^{-i\omega t}$$

with $V = -\frac{e}{mc} A_0 (\vec{\epsilon} \cdot p) e^{-ikx}$. For linearly polarized light, $\vec{\epsilon}$ and $A_0$ may be taken to be real, but this need not be the case. Specifically, complex $\vec{\epsilon}$ allow for treating circularly polarized light.
\[ w_{if} = \frac{2\pi}{\hbar} \left( \frac{eA_0}{mc} \right)^2 |(f | e^{ikx} \epsilon \cdot p | i)|^2 \delta(E_f - E_i - \hbar\omega) \]

where the transition rate is given just for the absorption case. Emission will be discussed later. Some comments about the $\delta$-function are appropriate. It may seem a remarkable coincidence for $\omega$ to have just the right frequency, however, if it does the strength of the transition is very large! It should be noted that we have set up the problem for a single plane wave. More practically, the electromagnetic field will be a distribution of plane waves, and one has to integrate over that distribution. Several effects act to smear out the strength of $\delta$-function. For example:

a) natural line width: the excited states of the atom are not pure energy eigenstates, since they can decay to lower energy states by emission of a photon. As a result, the energy is not well defined.

b) collision broadening: in a gas the atoms are constantly suffering collisions with other atoms. These collisions can alter the state of the atom, or at least act to continually perturb it. Again, the result is to smear out the energies of the bound states.

c) doppler broadening: in any realistic system the atoms will be moving around with a characteristic velocity. The velocity of the atom smooths out the photon energy distribution, so even if there were line features in the radiation field, they would be smeared out by the doppler effect.

As in the discussion of Fermi's golden rule, there is still a phase space integral - but here it is over the density of initial state photons. The energy $\delta$-function gets used to select those initial photons which satisfy the energy condition. So, the total rate to excite atoms is

\[ \Gamma_{i\rightarrow f} = \int d\omega \rho(\omega) \omega_{if} \]

\[ = \frac{2\pi}{\hbar} \left( \frac{eA_0}{mc} \right)^2 |(f | e^{ikx} \epsilon \cdot p | i)|^2 \rho(\omega_{if}) \]

where $\rho(\omega)$ is the density of photons of energy $\hbar\omega$. From a classical perspective, the density of photons can be related to the power of the incident radiation beam.

\[ \text{Photons & the radiation field} \]

Although a classical plane wave is nice, another approach is to consider the radiation field as a collection of photons, described by mode functions, annihilation and creation operators. The states are represented by specifying the degree of excitation in Fock space. Accordingly, this picture is presented before moving to particular applications.

This material may be found in many books, including Merzbacher Chap 23, or almost any introductory book on field theory. Recalling the discussion describing quantization of sound on a string, a similar construction is made for the electromagnetic field, leading to the concept of photons.

The discussion here is brief, and no promise is made that all factors of $\hbar$, $c$, $2\pi$, etc correct.

\[ \text{modes of field. definition of annihilation and creation operators} \]

The energy is given by
\[ H = \int dV \frac{1}{8\pi} (E^2 + B^2) \]

where, in the absence of an electrostatic potential, \( E = -\frac{1}{c} \dot{A} \) and \( B = \nabla \times A \), and \( A \) is the vector potential. The energy can be reexpressed as a sum over plane wave modes \( A = \sum_{k\lambda} A_{k\lambda} e^{ik\cdot x} \). Here \( A_{k\lambda} \) is an amplitude, \( \epsilon_{k\lambda} \) is a vector with \( \epsilon_{k\lambda} \cdot k = 0 \) as required by \( \nabla \cdot E = 0 \). This enforces that the two polarization vectors are transverse. Since the polarization states can be chosen to be orthogonal \( \epsilon_{k\lambda} \cdot \epsilon_{k'\lambda'} = \delta_{\lambda\lambda'} \).

The Hamiltonian is then

\[ H = \int dV \frac{1}{8\pi} \sum_{k\lambda} \sum_{k'\lambda'} e^{ik\cdot x} e^{-ik'\cdot x} \left( \frac{1}{c^2} \epsilon_{k\lambda} \cdot \epsilon_{k'\lambda'} A_{k\lambda} \dot{A}_{k'\lambda'} + (k \cdot k' \epsilon_{k\lambda} \epsilon_{k'\lambda'} - k \cdot \epsilon_{k'\lambda'} k' \cdot \epsilon_{k\lambda}) A_{k\lambda} A_{k'\lambda'} \right) \]

where in the \( B^2 \) term, each \( \nabla \) pulls down a factor of \( ik \) from the plane wave exponential. Integrating over \( dV \) yields a \( \delta \)-function, which in turn allows the rest of the form to be simplified to that for a harmonic oscillator where \( A_{k\lambda} \) plays the role of a position coordinate.

\[ H = \int dV \frac{1}{8\pi c^2} \sum_{k\lambda} \sum_{k'\lambda'} \delta(k - k') \left( \frac{1}{c^2} \epsilon_{k\lambda} \cdot \epsilon_{k'\lambda'} A_{k\lambda} \dot{A}_{k'\lambda'} + (k \cdot k' \epsilon_{k\lambda} \epsilon_{k'\lambda'} - k \cdot \epsilon_{k'\lambda'} k' \cdot \epsilon_{k\lambda}) A_{k\lambda} A_{k'\lambda'} \right) \]

\[ = \int dV \frac{1}{8\pi c^2} \sum_{k\lambda} \sum_{k'\lambda'} \frac{1}{c^2} \epsilon_{k\lambda} \cdot \epsilon_{k'\lambda'} \dot{A}_{k\lambda} \dot{A}_{k'\lambda'} + (k^2 \epsilon_{k\lambda} \epsilon_{k'\lambda'} - k \cdot \epsilon_{k'\lambda'} k \cdot \epsilon_{k\lambda}) A_{k\lambda} A_{k'\lambda'} \]

\[ = \int dV \frac{1}{8\pi c^2} \sum_{k\lambda} \sum_{k'\lambda'} \delta_{\lambda\lambda'} (\dot{A}_{k\lambda} \dot{A}_{k'\lambda'} + \omega^2 A_{k\lambda} A_{k'\lambda'}) \]

\[ = \int dV \frac{1}{8\pi c^2} \sum_{k\lambda} \left( \dot{A}_{k\lambda}^2 + \omega^2 A_{k\lambda}^2 \right) \]

where \( \omega = kc \). Once it has been established that \( k' = k \), one may use \( \epsilon_{k\lambda} \cdot \epsilon_{k'\lambda'} = \delta_{\lambda\lambda'} \) and \( \epsilon_{k\lambda} \cdot k = 0 \). The end result is a set of harmonic oscillators, so one can define annihilation operators \( a_{k\lambda} = N_{k\lambda} (\omega_k A_{k\lambda} + i \dot{A}_{k\lambda}) \) and creation operators \( a_{k\lambda}^\dagger \), where \( N_{k\lambda} \) is a normalization factor to be determined. There is a number operator \( N_{k\lambda} = a_{k\lambda}^\dagger a_{k\lambda} \) for each mode, and the energy should be given by

\[ H = \sum_{k\lambda} \omega_k (N_{k\lambda} + \frac{1}{2}) \]

\[ = \sum_{k\lambda} \omega_k N_{k\lambda} \]

In the last line an infinite zero-point energy has been dropped, and it is noted that the energy depends only on the momentum, but not on the polarization state. The eigenstates of this system may be described by a Fock space for photons, i.e. specifying each of the \( N_{k\lambda} \). The total number of photons in the system being

\[ N = \sum_{k\lambda} N_{k\lambda} \]

**Normalization**

The normalization of \( a_{k\lambda} \) can be determined by comparing the two forms for \( H \). Mode by mode

\[ \frac{1}{8\pi c^2} \left( \dot{A}_{k\lambda}^2 + \omega_k^2 A_{k\lambda}^2 \right) = \omega_k N_{k\lambda} = \omega_k N_{k\lambda}^2 (\dot{A}_{k\lambda}^2 + \omega_k^2 A_{k\lambda}^2) \]

or

\[ H = \sum_{k\lambda} \omega_k (N_{k\lambda} + \frac{1}{2}) \]

\[ \omega_k N_{k\lambda} = \omega_k N_{k\lambda}^2 \left( \dot{A}_{k\lambda}^2 + \omega_k^2 A_{k\lambda}^2 \right) \]
\[ N_k = \sqrt{\frac{1}{8\pi c^2 \omega_k}} \]

There is also a normalization factor associated with the spatial volume over which the modes are defined. For a periodic box this is a factor of \(1/L^{3/2}\). This factor will be discussed later, but for now it is noted that it should drop out of calculations of cross-sections and rates.

**Time dependence and the field**

The time dependence of the operators is given in the Heisenberg notation,

\[ a(t) = e^{-i\omega t} a(t = 0) \quad \text{and} \quad a^\dagger(t) = e^{i\omega t} a^\dagger(t = 0) \]

Putting together all the above elements, the field \( \vec{A} \) to be used in the interaction Hamiltonian is

\[ \vec{A} = \sum_{k \lambda} a_{k \lambda} \epsilon_{k \lambda} e^{i(k \cdot x - \omega t)} + a^\dagger_{k \lambda} \epsilon^*_{k \lambda} e^{-i(k \cdot x - \omega t)} \]

(5/20/04 - Comparing to the mode expansion above, these notes do not fully justify the appearance of the conjugate term in this field definition)

**Matrix elements with both atomic and radiative degrees of freedom**

Having quantized the electromagnetic field, a variety of electromagnetic processes with atoms can be revisited in terms of emission or absorption of photons. The interaction hamiltonian \( p \cdot A \) is now

\[ H_I = p \cdot A = p \cdot \left( \sum_{k \lambda} a_{k \lambda} \epsilon_{k \lambda} e^{i(k \cdot x - \omega t)} + a^\dagger_{k \lambda} \epsilon^*_{k \lambda} e^{-i(k \cdot x - \omega t)} \right) \]

This interaction hamiltonian acts between states defined both by their atomic (or electronic) degrees of freedom, and by the radiative degrees of freedom. The radiative states are defined in terms of Fock space, with the spatial dependence of the modes incorporated into the atomix matrix element. Thus a matrix element for the atomic transition \( i \rightarrow f \), by absorption of a photon from mode \( k \lambda \) would be written as

\[ \langle f, n_{k \lambda} - 1 | H_I | i, n_{k \lambda} \rangle = \left( \sum_{k' \lambda'} \langle f | p \cdot \epsilon_{k' \lambda'} e^{i(k' \cdot x - \omega t')} | i \rangle \left( n_{k \lambda} - 1 \right) a_{k' \lambda'} \epsilon_{k \lambda}^* e^{-i(k' \cdot x - \omega t')} \right) \]

\[ = \sum_{k' \lambda'} \langle f | p \cdot \epsilon_{k' \lambda'} e^{i(k' \cdot x - \omega t')} | i \rangle \sqrt{n_{k \lambda}} \delta_{k k'} \delta_{\lambda \lambda'} \]

\[ = \langle f | p \cdot \epsilon_{k \lambda} e^{i k \cdot x} | i \rangle \sqrt{n_{k \lambda}} e^{-i\omega t} \]

where the photon creation operators were dropped because this is an absorption process. The factor of \( e^{-i\omega t} \) is treated as the time dependence of a perturbation, and results in an energy conserving \( \delta \)-function. When the matrix element is squared the factor \( n_{k \lambda} \) will give the intensity of the initial beam of photons (or the intensity of the that fourier mode of the radiation field), the spatial matrix element \( \langle f | p \cdot \epsilon_{k \lambda} e^{i k \cdot x} | i \rangle \) describes the coupling of the initial and final electron states through the radiation field.
There is an asymmetry in the treatment of the electrons and the photons. The electrons are treated as a wavefunction and the photons are treated as a Fock space over the modes of the field. This asymmetry can be removed by treating the electronic degree of freedom as a field as well. In that case the wave functions play the role of modes for the electron field, and a fock space representation of the electron field will generate a factor of $\sqrt{n_i}$ to absorb an electron from the initial mode and a factor of $\sqrt{1 - n_f}$ to create an electron in the final mode. If the initial mode is occupied and the final mode is empty, then both factors are unity, and the above result is unchanged in form. The interpretation changes, though, in that the matrix element $\langle f | p \cdot \varepsilon \cdot \varepsilon | i \rangle$ is considered to be just a spatial overlap function of the modes describing the strength of $H_f$ to change the state of the system. The state itself is described by the occupation numbers in Fock space.

- **The matrix element**

The next step in the discussion of radiative transitions is to examine the matrix element $\langle f | e^{ik \cdot x} \cdot p | i \rangle$ for a few basic processes.

- **Atomic transitions**

Begin by considering the exponential $e^{ik \cdot x}$. For atomic transitions, it is reasonable to estimate the wavevector as having a magnitude of order 1 Rydberg, $k \sim E_0 = \frac{e^2}{2a_0}$ where $a_0$ is the Bohr radius of the atom. At the same time, evaluated within the matrix element, $x$ is expected to be of order the size of the atom, $x \sim a_0$. Combined $k \cdot x \sim \frac{e^2}{a_0} a_0 = e^2 = \frac{1}{137}$. (All working in "natural units" $\hbar = c = 1$). Since $k \cdot x$ is small, it is reasonable to expand $e^{ik \cdot x} = 1 + ik \cdot x ..., and approximate $e^{ik \cdot x} \approx 1$. The matrix element is then

$$\langle f | \epsilon \cdot p | i \rangle = \epsilon \cdot \langle f | p | i \rangle$$

$$= \frac{i m}{\hbar} \epsilon \cdot \langle f | [H_0, x] | i \rangle$$

$$= \frac{i m}{\hbar} (E_f - E_i) \epsilon \cdot \langle f | x | i \rangle$$

$$= im \omega_f \epsilon \cdot \langle f | x | i \rangle$$

where we have used $[H_0, x] = \frac{p^2}{2m}, x = -i \frac{\hbar}{m} p$, and evaluated $H_0$ on the unperturbed basis states. Note that the matrix element has been written in terms of $\epsilon \cdot x$. This can be evaluated in cartesian coordinates

$$\epsilon \cdot x = \epsilon_x x + \epsilon_y y + \epsilon_z z$$

or in terms of tensors

$$\epsilon \cdot x = \epsilon_z x_0 + \epsilon_+ x_+ + \epsilon_- x_-$$

where $x_0 = z, x_+ = \frac{1}{\sqrt{2}} (x + iy)$, and similarly for $\epsilon$. If using spherical tensors, the quantization axis is the direction of the initial photon. The matrix element evaluated here is the E1 electric dipole matrix element. Higher order terms E2, etc arise from including more terms in the expansion of $e^{ik \cdot x}$, but the strength of the transition is suppressed by factors of $e^2$.

Expressed in terms of $x_\pm$, the atomic selection rules $m_f = m_i \pm 1$ and $j_f = (j_i + 1, j_i$, or $j_i - 1)$ are a direct consequence of the Wigner-Eckart theorem.
**Bound-free transitions**

In this case, the final state is an outgoing wave. One can work in an outgoing basis projected onto plane waves, so that

\[
\langle f | e^{i k \cdot x} \epsilon \cdot p | i \rangle \rightarrow \langle k_f | e^{i k \cdot x} \epsilon \cdot p | i \rangle = \langle k_f | p \cdot \epsilon e^{i k \cdot x} | i \rangle = k_f \cdot \epsilon \langle k_f | e^{i k \cdot x} | i \rangle = k_f \cdot \epsilon \int dV \langle k_f | x \rangle e^{i k \cdot x} \langle x | i \rangle = k_f \cdot \epsilon \int dV e^{i(k_f \cdot x)} \psi_f(x)
\]

where \( k \) is the incident photon momentum, and \( k_f \) is the outgoing electron momentum. The movement of \( p \) to the left is justified by the transverse nature of the photon, \( k \cdot \epsilon = 0 \), and the next step follows by evaluating \( \langle k_f | p = \langle k_f | k_f \rangle \). The eigenvalue can then be taken out of the matrix element, which is evaluated as a spatial overlap integral. The preference is to eject the electron along the direction of polarization of the electric field.

**Cross-sections and flux normalization**

The concept of a cross-section arises when evaluating the rate at which the intensity of a beam is attenuated by scattering or absorption. The experimental situation is easy to setup and allows one to probe the nature of the beam, the scattering particles, and/or the nature of the interaction between the two. A typical setup would be to have a beam of particles incident from the left upon a target, or collection of targets, which absorb or scatter the beam. If the targets are well separated, but localized with respect to the beam size, they can typically be treated individually. If there exists a spatial correlation of the targets, then coherent scattering effects may be observed, but for the moment only single scatterers are considered.

The beam is defined by a flux of particles \( \phi = n v \), where \( n \) is the density and \( v \) is the velocity of particles in the beam. Imagine a target of well defined area \( A \) which occupies part of the beam. Then the rate at which particles hit the target is

\[
\Gamma = A \phi = n v A
\]

Next, imagine that the target is not defined by a sharp profile, but still there is a measurable rate at which particles are taken out of the beam. Then the cross-sectional area of the target is defined by

\[
\sigma = \frac{\Gamma}{\phi} = \frac{\Gamma}{n v}
\]

**Flux normalization - classical EM wave**

For the quantum calculation one needs to define the proper boundary condition to define the beam and the target. For definiteness, consider three treatments of a beam of electromagnetic energy. In the first, the beam is treated as a classical plane which causes a perturbation. The vector potential is

\[
\vec{A} = 2 A_0 \epsilon \cos(k \cdot x - \omega t) = 2 A_0 \epsilon (e^{i(k \cdot x - \omega t)} + e^{-i(k \cdot x - \omega t)})
\]
where $\hat{e}$ defines the polarization with unit normalization, and $A_0$ gives the amplitude. The time averaged energy density is

$$U = \frac{1}{16\pi} (E^2 + B^2) = \frac{1}{2\pi} \frac{\omega^2}{c^2} A_0^2 = n\omega$$

where in the last the step the energy density is interpreted as a number density of photons, each with energy $\omega$. This defines the number density as

$$n = \frac{1}{2\pi} \frac{\omega}{c} A_0^2$$

and the flux

$$\phi = nc = \frac{1}{2\pi} \frac{\omega}{c} A_0^2$$

Note that $A_0$ also shows up as the strength of the perturbation, and hence is present in the matrix element $V_{if} \sim A_0$. The transition rate scales as $\Gamma \sim |V_{if}|^2 A_0^2$. The cross-section is independent of the intensity of the beam

$$\sigma = \frac{\Gamma}{\phi} \sim \frac{A_0^2}{A_0^2}.$$  

### Flux normalization - particle beam

Alternatively, the beam can be treated as part of the incident state. For a calculation involving the scattering or absorption of particles a typical application treats the initial state as a plane wave

$$\langle x | i \rangle = \sqrt{N / V} \ e^{ikx}$$

where $N / V$ is normalized to the density of particles in the beam. In this case, the velocity is given by

$$\langle v \rangle = \frac{\langle \hat{p} \hat{p} \rangle}{\langle \hat{p} \rangle} = \frac{\hbar k}{m}$$

so the flux is

$$\phi = \frac{\hbar k}{m} \frac{N}{V}$$

Meanwhile, the normalization of the transition rate also includes the amplitude of the plane wave, which when the matrix element is squared also yields a factor of $\frac{N}{V}$. Note, however, that although the the density drops out of the calculation, the cross-section has a factor of $\frac{1}{\nu}$ due to the factor of $\frac{1}{\phi}$ in the definition of $\sigma$.

### Flux normalization - photons and other quantized beams

In this case, the beam can be described by several quanta occupying the same mode. The normalization of the mode is nominally defined to correspond to one particle within the volume of the space, e.g. $1 / L^{3/2}$. The occupation of the state then gives the density of particles in the beam

$$n = \frac{N_i}{V} = \frac{\langle n_i \hat{a}^\dagger \hat{a} n_i \rangle}{V}$$
For the case of absorption, similar factors show up in the squared matrix element: a factor of $\frac{1}{\sqrt{V}}$ is included in the normalization of the mode function, whereas the factor of $\sqrt{N_f}$ results from operation of the annihilation operator involved in the absorption process. Specifically, the matrix element contains a term

$$\langle (n_{k\lambda})_i - 1 \mid a_{k\lambda} \mid (n_{k\lambda})_i \rangle \langle \ell \mid \frac{1}{L^3} e^{ik\cdot x} \mid i \rangle = \frac{1}{L^3} \sqrt{(n_{k\lambda})_i} \langle \ell \mid e^{ik\cdot x} \mid i \rangle$$

and the rate therefore scales as

$$\Gamma \sim \frac{1}{V} (n_{k\lambda})_i$$

which cancels corresponding factors in the flux normalization.

Note I: In reactions where a photon is produced the corresponding matrix element involves $a^\dagger$, and the squared amplitude is $1 + (n_{k\lambda})_i$, corresponding to spontaneous and stimulated emission.

Note II. For an application involving a fermionic beam, the situation is somewhat different. First, there must be an even number of annihilation and or creation operators in the matrix element, otherwise initial and final angular momentum will differ by a $\frac{1}{2}$-integral amount. Second, the corresponding amplitudes will yield factors of $(n_{k\lambda})_i$ for the annihilation of any initial state fermion and $1 - (n_{k\lambda})_f$ for the creation of any final state fermions. The absorption factors are consistent with common sense and proportional to the intensity of the beam. The final state factors cause a suppression of transition rates and effective cross-sections in cases where the final states are occupied. As a trivial example, atomic transitions are not allowed to states that are already occupied. In dense materials (metals, white dwarfs, neutron stars, big bang nucleosynthesis), scattering to occupied states is suppressed.

**phase space**

The usual way to proceed is to take the system to be a box of side $L$ and volume $L^3$ with periodic boundary conditions. Then the eigenstates are denoted by $(n_x, n_y, n_z)$ with each of the $n$ taking on all integer values, and the wave vector is given by $\vec{k} = \frac{2\pi}{L} \vec{n}$. To proceed, consider the number of states within a volume element of $k$-space. Since the spacing depends on $L$, each state occupies a volume of $\left(\frac{2\pi}{L}\right)^3$, or the density of states is

$$\rho(k) = \left(\frac{L}{2\pi}\right)^3$$

The enumeration is then given by

$$\sum_f \sum_k \sim (\frac{L}{2\pi})^3 \int d^3k$$

It may look as if the phase space becomes infinite as the box gets bigger. This is an illusion though, since the normalization of each state decreases as $\frac{1}{\sqrt{V}} = L^{-3/2}$. When the matrix element is squared, the normalization gives exactly a factor of $\frac{1}{L^3}$. In the calculation of $\Gamma$, the factors of $L$ drop out. Recognizing this fact, take the plane wave states to be $\langle x \mid k_f \rangle = e^{ik_f \cdot x}$, and the sum over states to be

$$\sum_f \sim \frac{1}{(2\pi)^3} \int d^3k = \frac{1}{(2\pi)^3} \int k_f^2 dk_f d\Omega$$

Using $E = \frac{\hbar^2 k^2}{2m}$, or $dE = \frac{\hbar^2}{m} k dk$. This allows the phase space integral to be rewritten as
\[ \sum_f \rightarrow \frac{1}{(2\pi)^3} \int k_f^2 \, dk_f \, d\Omega = \frac{1}{(2\pi)^3} \int \frac{m}{\hbar^2} \, k_f \, dE_f \, d\Omega \]

If the matrix element is independent of angle, then the phase space simplifies a bit further since \( d\Omega = 4\pi \), and

\[ \sum_f \rightarrow \frac{1}{2\pi^2} \int \frac{m}{\hbar^2} \, k_f \, dE_f = \int \rho(E_f) \, dE_f \]

with \( \rho(E_f) = \frac{1}{2\pi^2} \frac{m}{\hbar^2} \, k_f = \frac{1}{2\pi^2} \frac{m}{\hbar^2} \sqrt{2mE_f} \)

- **phase space for photons**

The discussion proceeds as for the electron phase space, except the photon is massless. The sum over states is

\[ \sum_{k\lambda} \rightarrow \left( \frac{k}{2\pi} \right)^3 \sum_{\lambda} \int d^3 k \]

Dropping the \( L^3 \) as above, and using \( E = \hbar c \) for photons,

\[ \sum_{k\lambda} \rightarrow \frac{1}{(2\pi)^3} \int \frac{m}{\hbar^2} \, k_f \, dE_f \, d\Omega = \frac{1}{(2\pi)^3} \int E^2 \, dE \, d\Omega \]

If the matrix element is independent of the outgoing direction and photon spin, then

\[ \sum_{k\lambda} \rightarrow \frac{1}{\pi^2} \int E^2 \, dE \]

- **Processes**

- **photoelectric effect**
- **matrix element for ionization (photoelectric effect) bound-free transitions**
- **spontaneous decay**
- **detailed balance**
- **rate balance - saha equation**

- **Application to simple scattering**

As developed here, time dependent perturbation theory can be applied to perform simple scattering applications. As an initial state, consider a plane wave. As a final state one can take another plane wave, or an outgoing spherical wave. When scattering into a final state plane wave one typically determines the form factor of the potential. When scattering into outgoing spherical waves, one typically expresses the initial state as a sum over incoming spherical waves and performs a "partial wave" analysis. Given the limited time available, the treatment here will be confined to the former case in what is commonly called the Born approximation.
- **Born approximation**

Consider the problem of perturbation theory in the case where the system consists of an initial plane wave and in the presence of a scattering potential. The transition rate out of the state $|i\rangle$ is given by

$$\Gamma_i = \frac{1}{(2\pi)^2} \int d\mathbf{k}_f \frac{2\pi}{\hbar} |V_{if}|^2 \rho(E_f) \delta(E_f - E_i)$$

where, for a spherically symmetric potential $V(\mathbf{x}) = V(r)$

$$V_{if} = \langle k_f | V | k_i \rangle$$
$$= \int d^3 x \ e^{i(k_f-k_i)\cdot x} V$$
$$= 2\pi \int r^2 \sin[\theta] \, dr \, d\theta \, e^{iqr \cos[\theta]} \, V$$
$$= 4\pi \int r^2 \, dr \ \frac{(e^{iqr} - e^{-iqr})}{2iqr} \, V$$
$$= \frac{4\pi}{q} \int r \, dr \ \sin[qr] \, V$$
$$\equiv F(q)$$

Here $q = k_f - k_i$ is the momentum transfer. The matrix element only depends on the momentum transfer, not on the initial or final state separately. $F(q)$ is called the form factor for the potential.

- **Yukawa & Coulomb potentials**

(e.g. Sakurai 7.2)

The Coulomb potential is $V = \frac{1}{r}$, which does not have a well behaved form factor. One way to deal with this is to give the potential a finite range

$$V_\mu(r) = \frac{e^{-\mu r}}{r}$$

This form is known as a Yukawa potential. It was invented by Yukawa, in an attempt to model the forces that bind protons and nucleons into nuclei. The parameter $\mu$ has dimensions of mass. For nuclear physics, the interpretation is that $\mu$ is the mass of the $\pi$-meson. For an application to the Coulomb potential, $\mu$ is a parameter that allows one to "regulate" the calculation. At the end of the calculation, take $\mu \to 0$. The form factor for $V_\mu$ is

$$F_\mu(q) = \frac{4\pi}{q} \int dr \ \sin[qr] \ e^{-\mu r}$$
$$= \frac{4\pi}{q^2 + \mu^2}$$

So the Coulomb potential has the form factor

$$F_C(q) = \frac{4\pi}{q^2}$$

- **Stuff**