

Lecture 2

4 Fermi's golden rule

Literature: R.L. Liboff, Introductory Quantum Mechanics (Fourth edition) (Addison Wesley), Chapter 13.6

Learning goals

- To know Fermi's golden rule: what does it describe, when is it valid.
- To be able to derive Fermi's golden rule.
- To know the semiclassical description of atom-light interaction at the microscopic level and understand the approximations used in the description.
- To be aware of the existence of sum rules.

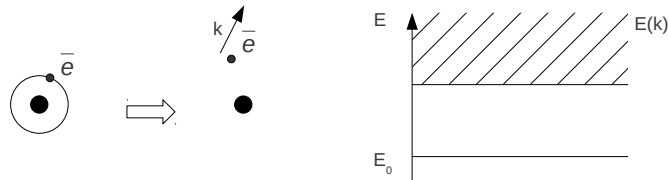


Figure 1: Example of a transition from an energy state E_0 to a continuum of states $E(k)$: the ionization of an atom. The electron, when removed from the atom, may have any momentum k . The possible energy states are given by the continuum dispersion of a free particle $E(k)$.

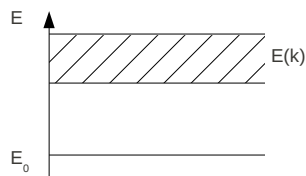


Figure 2: An energy state E_0 and an energy band characterized by some dispersion $E(k)$.

A particularly important result from the TDPT is the Fermi's golden rule (also called the Golden Rule). It gives transition rates in case the perturbation couples a state into a *continuum*, or a *band*, of states. This can be the case for instance when an atom is ionized, i.e. the electron is transferred from an electronic ground state of an atom into a free electron state which can have a continuum of

possible momentum states. Another example is a molecule in an electronic ground state, coupled by light field with a band of electronic and vibrational states. There would be an endless list of examples; this is actually what made the famous physicist Enrico Fermi to call this result as "Golden Rule".

Important: Fermi's golden rule is based on first order perturbation theory. So, it assumes that the perturbation is weak. For strong perturbations (strong coupling) it may not be valid any more.

Let us derive Fermi's golden rule. In Lecture 1, we obtained the first order TD perturbation theory result, in case of harmonic perturbation, from the transition probability amplitude from the state l to the state k (we now include λ in H'_{kl} , i.e. $H'_{kl} \equiv \lambda H'_{kl}$):

$$\langle k|\psi(t)\rangle_I \approx -i2H'_{kl} \left[\frac{e^{i(E_k - E_l - \hbar\omega)t/(2\hbar)} \sin\left(\frac{E_k - E_l - \hbar\omega}{2\hbar}t\right)}{E_k - E_l - \hbar\omega} + \frac{e^{i(E_k - E_l + \hbar\omega)t/(2\hbar)} \sin\left(\frac{E_k - E_l + \hbar\omega}{2\hbar}t\right)}{E_k - E_l + \hbar\omega} \right]. \quad (4.1)$$

We now include the coupling λ in H'_{kl} , i.e. $H'_{kl} \equiv \lambda H'_{kl}$. We discussed the resonant and non-resonant terms. Let us consider only the resonant processes. Note that whenever we are considering only two states and the resonant processes, we are doing the so-called two-level approximation. It assumes that it is sufficient to consider only two of the many possible electronic transitions in an atom/molecule/semiconductor if the frequency of the field is sufficiently close to only one of the transition energies, see Figure 3.

The transition probability becomes (let us denote $(E_k - E_l)/\hbar = \omega_{kl}$)

$$P_{lk} \approx \frac{4|H'_{kl}|^2}{\hbar^2(\omega_{kl} - \omega)^2} \sin^2\left(\frac{1}{2}(\omega_{kl} - \omega)t\right). \quad (4.2)$$

Now, we want to consider not only the transition from the state l to the state k , but the transition from the state l to a continuous band of energy states. The number of states within an energy interval from E_k to $E_k + dE_k$ is given by

$$dN = g(E_k)dE_k, \quad (4.3)$$

where $g(E_k)$ is the density of states. The probability that a transition occurs to a state in a band of width 2Δ centered at E_k is

$$\bar{P}_{lk} = \int_{E_k - \Delta}^{E_k + \Delta} g(E'_k) P_{lk} dE'_k. \quad (4.4)$$

Now we can insert P_{lk} from Equation (4.2). With the definition $2\hbar\beta \equiv (E'_k - E_l - \hbar\omega)t = \hbar(\omega_{kl} - \omega)t$ the result becomes

$$\bar{P}_{lk} = \int_{E_k - \Delta}^{E_k + \Delta} g(E'_k) \frac{|H'_{kl}|^2}{\hbar^2} \frac{\sin^2 \beta}{\beta^2/t^2} dE'_k. \quad (4.5)$$

When E_l , t and ω are fixed, we have

$$dE'_k = \frac{2\hbar d\beta}{t}. \quad (4.6)$$

Furthermore, with this change of variable the integration limits become

$$\pm\delta \equiv \frac{(E_k - E_l - \hbar\omega \pm \Delta)t}{2\hbar} = \frac{(\omega - \omega_{kl})t}{2} \pm \frac{\Delta t}{2\hbar}. \quad (4.7)$$

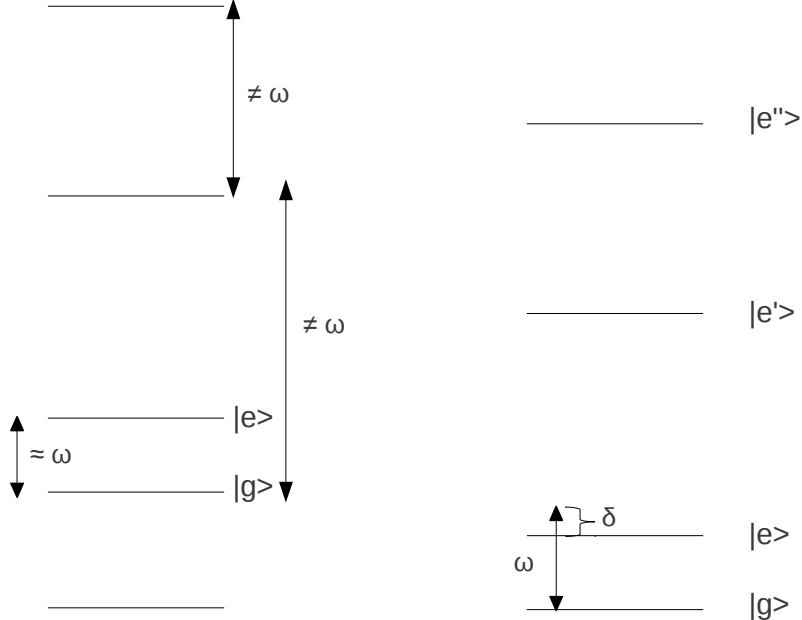


Figure 3: The two-level approximation: the energy $\hbar\omega$ corresponding to the field of frequency ω is close to only one of the possible transition energies. Note that even when the field frequency ω can be slightly detuned from the transition in question, i.e. the detuning $\delta = \omega - (E_e - E_g)$ is non-zero, the field frequency can still be so far from the other electronic transitions that the two-level approximation stays valid. Similar approximation can be done also when one has energy bands, not only energy levels.

The probability is now

$$\bar{P}_{lk} = \frac{2t}{\hbar} \int_{-\delta}^{+\delta} g(E'_k) |H'_{kl}|^2 \frac{\sin^2 \beta}{\beta^2} d\beta. \quad (4.8)$$

Since $\frac{\sin^2 \beta}{\beta^2}$ is a rapidly decaying function in β , c.f. Figure 4, we can approximate the integration limits $\pm\delta$ by $\pm\infty$. Note that in δ , the term $\omega - \omega_{kl}$ can become small when we are reasonably close to the resonance, $\omega \sim \omega_{kl}$. The approximation of setting the intergration limits to infinity is the better the longer is the time of probing t and/or larger the bandwidth Δ . Having large bandwidth (continuum) and long probing times is thus essential when applying the Fermi's golden rule. Often the density of states $g(E'_k)$ and the transition matrix element $|H'_{kl}|^2$ are slowly varying functions of E'_k and can therefore be taken out of the integration. The remaining integral can be calculated analytically and gives simply π . We have thus derived

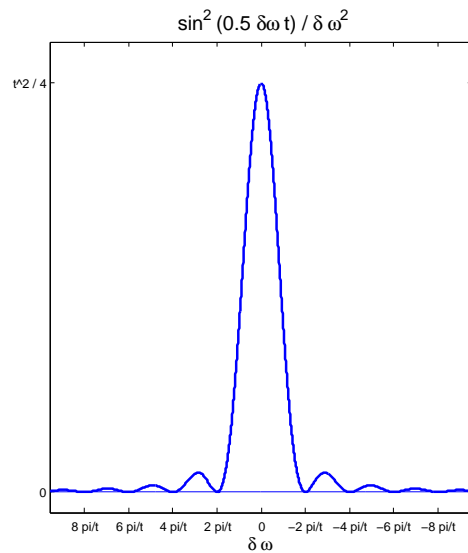


Figure 4: Rapid decay of a function of the form $\sin^2(x)/x^2$.

the **Fermi's golden rule result for the transition probability**:

$$\bar{P}_{lk} = \frac{2\pi t}{\hbar} g(E_k) |H'_{kl}|^2. \quad (4.9)$$

And the **transition rate** $\bar{\Gamma}_{lk} = \bar{P}_{lk}/t$ becomes

$$\bar{\Gamma}_{lk} = \frac{2\pi}{\hbar} g(E_k) |H'_{kl}|^2. \quad (4.10)$$

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5 Atom-Radiation Interaction

Literature: R.L. Liboff, Introductory Quantum Mechanics (Fourth edition) (Addi-

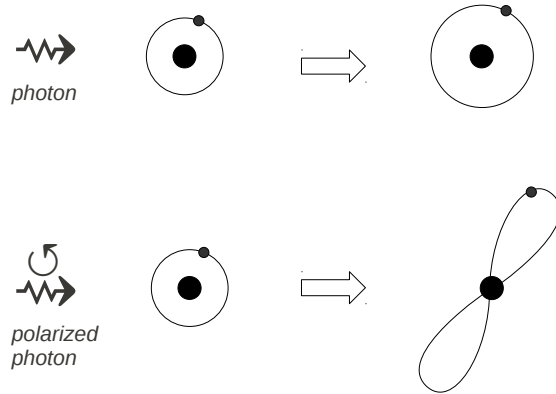


Figure 5: Electromagnetic radiation can cause the electron of an atom to go from one electronic state to another. If the radiation carries angular momentum, e.g. circularly polarized light, corresponding angular momentum change should occur also in the transition.

Now we will consider, microscopically, the interaction between radiation and atoms (can be easily extended for molecules, semiconductors, etc.). Frequencies from radio frequencies up to ultraviolet typically match the energies between the electronic energy levels of the atom. So we consider the interaction of the electrons of the atom with the radiation. An electron in an electromagnetic field with vector potential \mathbf{A} and electric potential $V(\mathbf{r})$ has the Hamiltonian

$$\hat{H} = \frac{1}{2m} [\hat{\mathbf{p}} - e\mathbf{A}(\mathbf{r}, t)]^2 + V(\mathbf{r}). \quad (5.1)$$

(Remember that the electric field $\mathbf{E} = -\nabla\varphi - \frac{\partial\mathbf{A}}{\partial t}$, and the magnetic field $\mathbf{B} = \nabla \times \mathbf{A}$. A change of the gauge can always be done $\mathbf{A} \rightarrow \mathbf{A} + \nabla\psi$, $\varphi \rightarrow \varphi - \frac{\partial\psi}{\partial t}$.) Note: this lecture follows the derivation in Liboff, but it is presented in SI units (which we use throughout this lecture) while in Liboff cgs units are used. If one starts from cgs units, the equivalent formula in SI units can be obtained by the replacements $\mathbf{E} \rightarrow \sqrt{4\pi\epsilon_0}\mathbf{E}$, $\mathbf{B} \rightarrow c\sqrt{4\pi\epsilon_0}\mathbf{B}$, $\mathbf{J} \rightarrow \sqrt{4\pi\epsilon_0}\mathbf{J}$, $\rho \rightarrow \rho/\sqrt{4\pi\epsilon_0}$, $q \rightarrow q/\sqrt{4\pi\epsilon_0}$, $\mathbf{A} \rightarrow c\sqrt{4\pi\epsilon_0}\mathbf{A}$, $\varphi \rightarrow \sqrt{4\pi\epsilon_0}\varphi$, where the quantities are the electric and magnetic fields, current density, charge density, charge, and the vector and scalar potentials, respectively, and c is speed of light and ϵ_0 the permittivity of free space.

5.1 Semiclassical description

Here we first treat the electron in the atom quantum mechanically (i.e. it has discrete energy states, the position and momentum of the electron are operators, etc.) and the field classically (i.e. there are no operators associated with the field, only complex numbers and vectors). This is called the semiclassical description. It is sufficient for explaining a large number, even most, of the atom-radiation interaction phenomena. Later in this course, however, we will treat also the field quantum mechanically, and that will lead to important phenomena that cannot be described semiclassically, like spontaneous emission. But let us now proceed with the semiclassical approach.

If the vector potential \mathbf{A} is taken as a classical field, the approach is called the semiclassical description. Now let us divide the Hamiltonian (5.1) into three parts:

$$\hat{H} = \hat{H}^{(0)} + \hat{H}' + \hat{H}'' . \quad (5.2)$$

Here, the unperturbed Hamiltonian is

$$\hat{H}^{(0)} \equiv \frac{\hat{\mathbf{p}}^2}{2m} + V(\mathbf{r}) . \quad (5.3)$$

The perturbation is

$$\hat{H}' \equiv -\frac{e}{2m} [\hat{\mathbf{p}} \cdot \mathbf{A} + \mathbf{A} \cdot \hat{\mathbf{p}}] . \quad (5.4)$$

We neglect the constant

$$\hat{H}'' \equiv \frac{e^2}{2m} \mathbf{A}^2 . \quad (5.5)$$

The matrix elements of \hat{H}' (important, e.g., in perturbation theory) are

$$\langle n' | \hat{H}' | n \rangle = -\frac{e}{2m} \int \psi_{n'}^* (\hat{\mathbf{p}} \cdot \mathbf{A} + \mathbf{A} \cdot \hat{\mathbf{p}}) \psi_n d\mathbf{r} . \quad (5.6)$$

Remember that

$$\hat{\mathbf{p}} \cdot \mathbf{A} \psi_n = \frac{\hbar}{i} \nabla \cdot (\mathbf{A} \psi_n) = \frac{\hbar}{i} [\psi_n (\nabla \cdot \mathbf{A}) + (\mathbf{A} \cdot \nabla) \psi_n] . \quad (5.7)$$

In the Coulomb gauge this means

$$\nabla \cdot \mathbf{A} = 0 \Rightarrow \hat{\mathbf{p}} \cdot \mathbf{A} \psi_n = \frac{\hbar}{i} (\mathbf{A} \cdot \nabla) \psi_n \quad (5.8)$$

so that

$$\langle n' | \hat{H}' | n \rangle = -\frac{e}{m} \int \psi_{n'}^* \mathbf{A} \cdot \hat{\mathbf{p}} \psi_n d\mathbf{r} . \quad (5.9)$$

$$\langle n' | \hat{H}' | n \rangle = -\frac{e}{m} \int \psi_{n'}^* \hat{\mathbf{p}} \cdot \mathbf{A} \psi_n d\mathbf{r} \quad (5.10)$$

If we now take \mathbf{A} to be associated with the wavefunction of a photon with an energy $E = \hbar\omega$ we get (quantization of the field will be done later in the course but let us already use the concept of a photon, i.e. quantum of the field)

Emission:

$$\langle n' | \hat{H}' | n \rangle \rightarrow -\frac{e}{m} \langle n' ; \hbar\omega | \hat{\mathbf{p}} | n \rangle . \quad (5.11)$$

Absorption:

$$\langle n' | \hat{H}' | n \rangle \rightarrow -\frac{e}{m} \langle n' | \hat{\mathbf{p}} | \hbar\omega ; n \rangle . \quad (5.12)$$

5.2 Interaction with a plane electromagnetic wave

We now consider a typical case for the form (spatial and time dependence) of the radiation, namely the plane electromagnetic wave:

$$\mathbf{A}(\mathbf{r}, t) = \mathbf{e}A_0 \cos(\mathbf{k} \cdot \mathbf{r} - \omega t). \quad (5.13)$$

Here \mathbf{e} is a unit polarisation vector, and A_0 chosen so that the corresponding wave carries one photon per unit volume. Let us now do this normalization. The time-averaged energy density is

$$\langle U \rangle = \frac{1}{\mu_0} \langle B^2 \rangle = \epsilon_0 \langle E^2 \rangle. \quad (5.14)$$

Here μ_0 is the permeability of free space. With $B = \nabla \times \mathbf{A} \sim \dots e_z A_0 k_x \cos(\mathbf{k} \cdot \mathbf{r} - \omega t) + \dots$, the energy density is $\langle U \rangle = \frac{1}{2\mu_0} k^2 A_0^2$. If we have one photon per volume, then Equation (5.14) has to satisfy the conditions

$$\langle U \rangle = \frac{\hbar\omega}{V} = \frac{k^2 A_0^2}{2\mu_0}. \quad (5.15)$$

With $\omega = ck$ and $c^2 = 1/(\mu_0\epsilon_0)$ it leads to

$$A_0^2 = \frac{2\hbar}{\omega V \epsilon_0}. \quad (5.16)$$

We set $V = 1$ here.

Also, we split the field \mathbf{A} into two parts:

$$\mathbf{A} = \frac{A_0}{2} \mathbf{e} \left[e^{i(\mathbf{k}\cdot\mathbf{r}-\omega t)} + e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega t)} \right] \equiv \mathbf{A}_+ + \mathbf{A}_-, \quad (5.17)$$

where

$$\mathbf{A}_\pm = \frac{A_0}{2} \mathbf{e} e^{\pm i(\mathbf{k}\cdot\mathbf{r}-\omega t)} = \left(\frac{\hbar}{2\omega\epsilon_0} \right)^{\frac{1}{2}} \mathbf{e} e^{\pm i(\mathbf{k}\cdot\mathbf{r}-\omega t)}. \quad (5.18)$$

We define $\hat{\mathcal{H}}_\pm(\mathbf{r})$ as

$$\hat{H}' = \hat{\mathcal{H}}_\pm(\mathbf{r}) e^{\mp i\omega t} \quad (5.19)$$

and, like in Equations (5.11) and (5.12),

$$\langle n' | \hat{\mathcal{H}}_\pm | n \rangle = -\frac{e}{m} \left(\frac{\hbar}{2\omega\epsilon_0} \right)^{\frac{1}{2}} \langle n' | \mathbf{e} \cdot \hat{\mathbf{p}} e^{\pm i\mathbf{k}\cdot\mathbf{r}} | n \rangle. \quad (5.20)$$

Now we have the transition matrix element in a form that can be further evaluated. In the following, some approximations will be used in calculating it.

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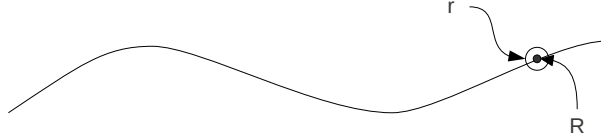


Figure 6: When the wavelength of the radiation is much larger than the scale of electronic orbitals in the atom, one can do the *dipole approximation*, that is, approximate the electric field amplitude at position r by the field amplitude at the atom center-of-mass position R .

5.3 The dipole approximation

For typical electronic transitions in atoms, the wavelength of the radiation is such that $\lambda \gg a_0$ where λ the light wavelength, a_0 Bohr radius. For the electron of the atom, the variation of the field over the radius of the atom is thus negligible, and one can replace $e^{i\mathbf{k}\cdot\mathbf{r}}$ by $e^{i\mathbf{k}\cdot\mathbf{R}}$ where \mathbf{R} is the center of mass position coordinate of the atom. This factor then becomes a simple constant instead of containing the position of the electron \mathbf{r} and can be taken out of the matrix element in Equation (5.20). This is called the dipole approximation. For the purposes of this lecture, we can assume the center of mass position of the atom fixed and choose $\mathbf{R} = 0$. Then the dipole approximation and the choice $R = 0$ amounts to saying that

$$e^{i\mathbf{k}\cdot\mathbf{r}} \simeq e^{i\mathbf{k}\cdot\mathbf{R}} = 1. \quad (5.21)$$

Therefore, Equation (5.20) becomes

$$\langle n' | \hat{\mathcal{H}}_{\pm} | n \rangle = -\frac{e}{m} \left(\frac{\hbar}{2\omega\epsilon_0} \right)^{\frac{1}{2}} \langle n' | \mathbf{e} \cdot \hat{\mathbf{p}} | n \rangle. \quad (5.22)$$

Let us use $\hat{\mathbf{r}}$ instead of $\hat{\mathbf{p}}$. (Note that $\hat{\mathbf{r}}$ is now an operator as well, namely the position operator for the electron. In this course, we do not always use hats for operators: you are supposed to think/remember yourself what is an operator, what is just a number. Sometimes we, however, emphasize that something is an operator by using the hat-symbol, like here; this hopefully helps you to separate the electron position which is a quantum mechanical operator from the coordinate of the electromagnetic field, which is just a number when the field is treated classically (the semiclassical approximation).) For conjugate operators one has $[\hat{x}, \hat{p}_x^2] = 2i\hbar\hat{p}_x$ (**Exercise set 2**). Noting also that now $\hat{H}^{(0)}$ contains a term proportional to $\hat{\mathbf{p}}^2$ and the term $V(\mathbf{r})$ which commutes with $\hat{\mathbf{r}}$, one can write:

$$\hat{\mathbf{p}} = \frac{im}{\hbar} [\hat{H}^{(0)}, \hat{\mathbf{r}}] \quad (5.23)$$

$$\langle n' | \hat{\mathbf{p}} | n \rangle = \frac{im}{\hbar} \langle n' | \hat{H}^{(0)} \hat{\mathbf{r}} - \hat{\mathbf{r}} \hat{H}^{(0)} | n \rangle =$$

($|n\rangle$ is an eigenstate of $\hat{H}^{(0)}$)

$$= \frac{-im}{\hbar} (E_n^{(0)} - E_{n'}^{(0)}) \langle n' | \hat{\mathbf{r}} | n \rangle = -im\omega_{nn'} \langle n' | \hat{\mathbf{r}} | n \rangle \quad (5.24)$$

Here we choose the convention $\omega_{nn'} > 0$, i.e. assume $E_n^{(0)} > E_{n'}^{(0)}$. If we had $E_n^{(0)} < E_{n'}^{(0)}$, we would replace $\omega_{nn'}$ by $-\omega_{n'n}$.

Now we take into use a notation where in the state $|n, \mathbf{k}\rangle$ \mathbf{k} is a label, indicating absorption/emission. Equation (5.20) is then written as

$$\langle n' | \hat{\mathcal{H}}_+ | n, \mathbf{k} \rangle = \langle n', \mathbf{k} | \hat{\mathcal{H}}_- | n \rangle = ie (\hbar\omega_{nn'}^2 / (2\omega\epsilon_0))^{\frac{1}{2}} \langle n' | \mathbf{e} \cdot \hat{\mathbf{r}} | n \rangle \equiv \mathcal{H}_{nn'}. \quad (5.25)$$

We now use the Golden Rule of Equation (4.10)

$$\bar{\Gamma}_{l \rightarrow k} = \frac{2\pi}{\hbar} g(E_k) |H'_{kl}|^2. \quad (5.26)$$

Transition probability rate within the solid angle $d\Omega$ is

$$d\Gamma_{nn'} = \sum_{\mathbf{e}_i} \frac{2\pi}{\hbar} |\mathcal{H}_{n'n}|^2 \bar{g}(E_k) d\Omega, \quad (5.27)$$

where $\bar{g}(E) d\Omega$ is the density of states of photons emitted into the solid angle $d\Omega$ (these relations you can find from previous courses on electromagnetism or in textbooks)

$$Vg(\nu)d\nu = 2 \left[V \int \bar{g}(E) d\Omega \right] dE \Rightarrow g(\nu) = 2\bar{g}(E) \int d\Omega \frac{dE}{d\nu}. \quad (5.28)$$

(Note that for an electromagnetic field in a box, the following holds: $g(\nu) = 8\pi\nu^2/c^3 = 2\omega^2/(\pi c^3)$, $E = h\nu = \hbar\omega$, $dE/d\nu = \partial(h\nu)/\partial\nu = h$.) From Equation (5.28):

$$\bar{g}(E) = \frac{2\omega^2}{\pi c^3} \frac{1}{2h} \frac{1}{4\pi} = \frac{\omega^2}{\hbar(2\pi c)^3} \quad (5.29)$$

and, returning to Equation (5.27):

$$\begin{aligned} d\Gamma_{nn'} &= \sum_{\mathbf{e}_i} \frac{e^2 \omega_{nn'}^2 \omega}{8\pi^2 \hbar c^3 \epsilon_0} |\langle n', \mathbf{k} | \mathbf{e}_i \cdot \hat{\mathbf{r}} | n \rangle|^2 d\Omega \\ &= \sum_{\mathbf{e}_i} \frac{e^2 \omega_{nn'}^2 \omega}{8\pi^2 \hbar c^3 \epsilon_0} |\mathbf{e}_i \cdot \langle n', \mathbf{k} | \hat{\mathbf{r}} | n \rangle|^2 d\Omega. \end{aligned} \quad (5.30)$$

In the appendix is shown a figure which explains the integration over a solid angle in this case. The result becomes

$$d\Gamma_{nn'} = \frac{e^2 \omega_{nn'}^2 \omega}{8\pi^2 \hbar c^3 \epsilon_0} |\langle n', \mathbf{k} | \hat{\mathbf{r}} | n \rangle|^2 \sin^2 \vartheta d\Omega. \quad (5.31)$$

The integrated transition rate is

$$A_{nn'} = \int d\Gamma_{nn'} = \frac{1}{3\pi\epsilon_0} \frac{e^2 \omega_{nn'}^2 \omega}{\hbar c^3} |\langle n' | \hat{\mathbf{r}} | n \rangle|^2 = \frac{1}{3\pi\epsilon_0} \frac{\omega_{nn'}^2 \omega}{\hbar c^3} d_{nn'}^2. \quad (5.32)$$

Note that here the notation $|\langle n' | \hat{\mathbf{r}} | n \rangle|^2 = |\langle n' | \hat{x} | n \rangle|^2 + |\langle n' | \hat{y} | n \rangle|^2 + |\langle n' | \hat{z} | n \rangle|^2$ is used. In Equation (5.32) the dipole matrix element is defined as

$$d_{nn'}^2 = e^2 |\langle n' | \hat{\mathbf{r}} | n \rangle|^2. \quad (5.33)$$

Quite often it is assumed that the field frequency ω and the transition frequency $\omega_{nn'}$ are very close to each other, and one sets $\omega = \omega_{nn'}$ which makes the transition rate to be of the form

$$A_{nn'} = \frac{1}{3\pi\epsilon_0} \frac{\omega^3}{\hbar c^3} d_{nn'}^2. \quad (5.34)$$

For an atom with Z electrons, the total dipole matrix element becomes

$$d_{nn'} = e \langle n' | \hat{\mathbf{r}} | n \rangle \rightarrow e \langle n' | \sum_{i=1}^Z \hat{\mathbf{r}}_i | n \rangle. \quad (5.35)$$

The values of dipole matrix elements depend on the transition in question, and can be calculated if the wavefunctions of the states n' and n are known. Knowing the dipole matrix element $d_{nn'}$ and the field frequency ω (transition frequency $\omega_{nn'}$), the transition probability rate is then simply given by Equation (5.34) (or (5.32)).

5.4 Oscillator strength

Instead of the dipole matrix element, in some fields of physics and chemistry people often talk about the oscillator strength. They are related by a simple definition, the oscillator strength, where $d_{nn'}$ is from Equation (5.33), is the following:

$$f_{nn'} = \frac{2m\omega_{n'n}}{3\hbar} |\langle n' | \hat{\mathbf{r}} | n \rangle|^2 = \frac{2m\omega_{n'n}}{3\hbar e^2} d_{nn'}^2. \quad (5.36)$$

There exists the so called Thomas-Reiche-Kuhn sum rule which states

$$\sum_{n'} f_{nn'} = 1. \quad (5.37)$$

Compared to the dipole matrix element, the oscillator strength is normalized in a nice way such that the sum rule sums up to unity and not some constant. **Sum rules** are a very important concept in physics. They give general restrictions to quantities like transition rates. For instance, if one obtains, by some approximate methods, transition rates that do not sum up like the sum rules states, one knows that the approximation is not valid.

Let us derive the sum rule (5.37); many other sum rules are derived using a similar thinking:

$$\langle n | [\hat{x}, \hat{p}_x] | n \rangle = i\hbar \quad (5.38)$$

$$\sum_{n'} [\langle n | \hat{x} | n' \rangle \langle n' | \hat{p}_x | n \rangle - \langle n | \hat{p}_x | n' \rangle \langle n' | \hat{x} | n \rangle] = i\hbar \quad (5.39)$$

c.f. Equations (5.23) and (5.24)

$$\sum_{n'} \left[im\omega_{n'n} |\langle n' | \hat{x} | n \rangle|^2 - im\omega_{nn'} |\langle n' | \hat{x} | n \rangle|^2 \right] = i\hbar \quad (5.40)$$

$$\sum_{n'} \frac{2m\omega_{n'n}}{\hbar} |\langle n' | \hat{x} | n \rangle|^2 = 1 \Rightarrow \quad (5.41)$$

$$\sum_{n'} \frac{2m\omega_{n'n}}{3\hbar} |\langle n' | \hat{\mathbf{r}} | n \rangle|^2 = \sum_{n'} f_{nn'} = 1. \quad (5.42)$$

For Z electrons, using Equation (5.35):

$$\sum_{n'} f_{nn'} = Z. \quad (5.43)$$

