2-photon transitions

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26th May 2003

1 Perturbation theory

We start with a derivation of time-dependent perturbation theory employing Heisenberg's formalism. In the Heisenberg picture, the evolution of a system is determined by a unitary time-dependent operator U, obeying the following equation:

$$i\hbar\dot{U}(t,t_0) = HU(t,t_0), \tag{1}$$

where $\dot{U}$ denotes the time derivative $\partial U/\partial t$, and H is the (time-dependent) Hamiltonian of the system. The evolution operator satisfies the following relations:

$$\begin{aligned} U(t,t_0) &= U(t,t')U(t',t_0) && (2)\\ U(t,t_0)^\dagger &= U(t,t_0)^{-1} = U(t_0,t) && (3)\\ U(t_0,t_0) &= \mathrm{Id}, && (4) \end{aligned}$$

where Id represents the identity operator. In the following, we will not always write the (t,t_0) dependence of the evolution operator explicitly. Suppose that the Hamiltonian can be written as the sum of a time-independent and a time-dependent part:

$$H = H_0 + V(t). \tag{5}$$

Since H_0 is time-independent, the Schrödinger equation for H_0:

$$i\hbar\dot{U}^{(0)}(t,t_0) = H_0U^{(0)}(t,t_0), \tag{6}$$

implies that formally:

$$U^{(0)}(t,t_0) = \exp\{-iH_0(t-t_0)/\hbar\}. \tag{7}$$

We will now define the following operator:

$$\widetilde{U}(t,t_0) \stackrel{\mathrm{def}}{=} U^{(0)\dagger}(t,t_0)U(t,t_0). \tag{8}$$

We will start by investigating this operator, and end up with an expansion that solves (in principal) the Schrödinger equation for the complete Hamiltonian. Consider the time derivative of $\widetilde{U}$. Using Leibniz' product rule, we get

$$\begin{aligned} i\hbar\dot{\widetilde{U}} &= i\hbar\dot{U}^{(0)\dagger}U + i\hbar U^{(0)\dagger}\dot{U} && (9)\\ &= -H_0U^{(0)\dagger}U + U^{(0)\dagger}HU && (10)\\ &= U^{(0)\dagger}[H - H_0]U = U^{(0)\dagger}V(t)U && (11)\\ &= \widetilde{V}(t)\widetilde{U}. && (12) \end{aligned}$$

In the last step we defined $\widetilde{V}(t) = U^{(0)\dagger}V(t)U^{(0)}$. The third step is permitted, since any operator commutes with it's exponentiated version: $[A, e^A] = 0$. Eq. 12 may be integrated to yield a solution for $\widetilde{U}$:

$$i\hbar\int_{t_0}^{t}\frac{\partial}{\partial\tau}\widetilde{U}(\tau,t_0)\,\mathrm{d}\tau = \int_{t_0}^{t}\widetilde{V}(\tau)\widetilde{U}(\tau,t_0)\,\mathrm{d}\tau, \tag{13}$$

which yields:

$$\widetilde{U}(t,t_0) = 1 + (-i\hbar)^{-1}\int_{t_0}^{t}\widetilde{V}(\tau)\widetilde{U}(\tau,t_0)\,\mathrm{d}\tau. \tag{14}$$

Using Eq. 2 we find a recursion relation for Eq. 14:

$$\widetilde{U}(t,t_0) = 1+(i\hbar)^{-1}\int_{t_0}^{t}\mathrm{d}\tau_1\int_{t_0}^{\tau_1}\mathrm{d}\tau_2\widetilde{V}(\tau_1)+(-i\hbar)^{-1}\widetilde{V}(\tau_1)\widetilde{V}(\tau_2)\widetilde{U}(\tau_2,t_0). \tag{15}$$

Applying the same trick to $\widetilde{U}(\tau_2,t_0)$ recursively, and after some rewriting, we find:

$$\widetilde{U} = 1 + \sum_{n=1}^{\infty}\widetilde{U}^{(n)}, \tag{16}$$

where

$$\widetilde{U}^{(n)} = (-i\hbar)^{-n}\int_{t_0}^{t}\mathrm{d}\tau_1\int_{t_0}^{\tau_1}\mathrm{d}\tau_2...\int_{t_0}^{\tau_{n-1}}\mathrm{d}\tau_n\widetilde{V}(\tau_1)\widetilde{V}(\tau_2)...\widetilde{V}(\tau_n). \tag{17}$$

Using Eqs. 2, 3, and 8 it's easy to find the following equation from Eq. 17:

$$U = U^{(0)} + \sum_{n\geq 1}U^{(n)}, \tag{18}$$

where

$$\begin{aligned} U^{(n)} &= (-i\hbar)^{-n}\int_{t_0}^{t}\mathrm{d}\tau_1\int_{t_0}^{\tau_1}\mathrm{d}\tau_2...\int_{t_0}^{\tau_{n-1}}\mathrm{d}\tau_n\\ &\times\ U^{(0)}(t,\tau_1)\left(\prod_{i=1}^{n-1}V(\tau_i)U^{(0)}(\tau_i,\tau_{i+1})\right)V(\tau_n)U^{(0)}(\tau_n,t_0). && (19) \end{aligned}$$

Note that this expansion is in principal exact, and can be truncated to approximate the complete solution.

Suppose we start with a system in a known state $|i\rangle$, let it evolve for some time, and then determine it's state again. The chance of finding the system in some final state $|f\rangle$ is given by:

$$\mathcal{P}_{f\leftarrow i}(t) = |\langle f|U(t,t_0)|i\rangle|^2 \tag{20}$$

We now return to the Hamiltonian in Eq. 5. Assuming that the time-dependent part gives a small contribution, we may approximate $\mathcal{P}_{f\leftarrow i}(t)$ by taking $|i\rangle$ and $|f\rangle$ from the eigenspace $\mathcal{H}_0$ of H_0 and truncating the expansion at some level:

$$\begin{aligned}
\langle f|U(t,t_0)|i\rangle &= \langle f|U^{(0)}(t,t_0)|i\rangle \\
&+ (-i\hbar)^{-1}\int_{t_0}^{t} \mathrm{d}\tau\ \langle f|U^{(0)}(t,\tau)V(\tau)U^{(0)}(\tau,t_0)|i\rangle \\
&+ (-i\hbar)^{-2}\sum_m \int_{t_0}^{t}\mathrm{d}\tau_1 \int_{t_0}^{\tau_1}\mathrm{d}\tau_2 \\
&\times \langle f|U^{(0)}(t,\tau_1)V(\tau_1)U^{(0)}(\tau_1,\tau_2)|m\rangle\langle m|V(\tau_2)U^{(0)}(\tau_2,t_0)|i\rangle \\
&+ \text{higher order.}
\end{aligned} \tag{21}$$

If we assume that H_0 has a pure-point spectrum (which is in general not the case), then the sum $\sum_m |m\rangle\langle m| = \mathrm{Id}_{\mathcal{H}_0}$.

2 Electromagnetism

Here is a short overview of some classical electromagnetism, necessary to understand the perturbing potential in the next section. There are a number of unit conventions for the electro magnetic theory. Two well-known systems are the Gaussian unit system, and the rationalized MKS (Meter Kilogram Second) system. Throughout this section we will work in rationalized MKS units, since this facilitates conversion to atomic units. In this unit system we may also apply the relation:

$$\epsilon_0\mu_0 = 1/c^2 \tag{22}$$

In the appendix there is a short list of vector identities that will be used and some conversion factors. Vector fields and quantities are denoted in a bold-face font, scalar fields are designated with a lower-case Greek letter.

2.1 Maxwell's equations

The macroscopic Maxwell equations for the free field are given by:

$$\begin{aligned}
&(a)\ \nabla\cdot\mathbf{D} = \rho \qquad (b)\ \nabla\times\mathbf{E} = -\dot{\mathbf{B}} \\
&(c)\ \nabla\cdot\mathbf{B} = 0 \qquad (d)\ \nabla\times\mathbf{H} = \mathbf{J} + \dot{\mathbf{D}},
\end{aligned} \tag{23}$$

with

$$\mathbf{D} = \epsilon_0 \mathbf{E} + \mathbf{P} \stackrel{\text{def}}{=} \epsilon\, \mathbf{E} \tag{24}$$

$$\mathbf{H} = \tfrac{1}{\mu_0}\mathbf{B} - \mathbf{M} \stackrel{\text{def}}{=} \tfrac{1}{\mu}\mathbf{B}, \tag{25}$$

where $\mathbf{E}$ indicates the electric field, $\mathbf{D}$ the electric displacement field and $\mathbf{P}$ the polarization field of the medium. The symbol $\mathbf{B}$ indicates the magnetic field, $\mathbf{H}$ the magnetic displacement field, $\mathbf{J}$ the current density, and $\mathbf{M}$ is the magnetization of the medium. The definitions in Eqs. 24 and 25 are only valid for isotropic linear media. From here, we consider the Maxwell equations for the vacuum, which means $\mu = \mu_0$ and $\epsilon = \epsilon_0$.

2.2 Gauge invariance

It is possible to derive a unified description for the electric and magnetic fields. First observe that Eq. 23*(c)* and the vector identity Eq. 87 imply that $\mathbf{B}$ may be written as follows:

$$\mathbf{B} = \nabla \times \mathbf{A}, \tag{26}$$

the quantity $\mathbf{A}$ is called the *vector potential.* We can also relate the electric field to the vector potential:

$$\nabla \times \mathbf{E} = -\nabla \times \dot{\mathbf{A}} \Rightarrow \nabla \times (\mathbf{E} + \dot{\mathbf{A}}) = 0. \tag{27}$$

Employing Eq. 88 we may write:

$$\mathbf{E} = -\dot{\mathbf{A}} - \nabla\phi. \tag{28}$$

Where ϕ is called the *scalar potential.* The negative sign is just a convention. Furthermore:

$$\begin{aligned} \nabla \times \mathbf{H} = \frac{1}{\mu_0}\nabla \times (\nabla \times \mathbf{A}) &= \mathbf{J} + \epsilon_0 \frac{\partial}{\partial t}\left(-\dot{\mathbf{A}} - \nabla\phi\right) \\ \nabla(\nabla\mathbf{A}) - \nabla^2\mathbf{A} &= \mu_0\mathbf{J} + \epsilon_0\mu_0\ddot{\mathbf{A}} - \epsilon_0\mu_0\nabla\dot{\phi}, \end{aligned} \tag{29}$$

where Eq. 89 is employed in the second step on the left hand side. Finally we rewrite Eq. 29, and combine Eq. 23*(a)* and 28, to obtain the equations of motion for ϕ and $\mathbf{A}$:

$$\nabla^2\mathbf{A} - \frac{1}{c^2}\ddot{\mathbf{A}} - \nabla(\nabla\mathbf{A} + \frac{1}{c^2}\dot{\phi}) = -\mu_0\mathbf{J} \tag{30}$$

$$\nabla\dot{\mathbf{A}} + \nabla^2\phi = -\rho/\epsilon_0. \tag{31}$$

These coupled equations are completely equivalent with the original Maxwell equations. The equations can be uncoupled by using the fact that $\mathbf{A}$ can be augmented with the gradient of any differentiable scalar field λ without changing

the magnetic field. In fact, the Eqs. 30 and 31 are invariant under the following simultaneous mappings:

$$\mathbf{A} \mapsto \mathbf{A} + \nabla\lambda \tag{32}$$

$$\phi \mapsto \phi - \dot{\lambda}. \tag{33}$$

This freedom allows us to impose restrictions (gauges) to the equations of motion, in order to decouple Eqs. 30 and 31. In (special) relativistic calculations, the Lorentz condition is imposed:

$$\nabla\mathbf{A} + \frac{1}{c^2}\dot{\phi} = 0, \tag{34}$$

this yields the condition that

$$\nabla(\mathbf{A} + \nabla\lambda) - \frac{\partial}{\partial t}\left[\phi - \frac{1}{c^2}\dot{\lambda}\right] = \nabla\mathbf{A} - \frac{1}{c}\dot{\phi} = 0, \tag{35}$$

which implies

$$\nabla^2\lambda - \frac{1}{c^2}\ddot{\lambda} = \Box\lambda = 0. \tag{36}$$

The operator $\Box$ is called the d'Alambertian[1]. The equations of motion for $\mathbf{A}$ and ϕ are then reduced to:

$$\Box\mathbf{A} = -\mu_0\mathbf{J} \tag{37}$$

$$\Box\phi = -\rho/\epsilon_0, \tag{38}$$

where we used $\nabla\dot{\mathbf{A}} = -1/c^2\ddot{\phi}$ in the second equation. In non-relativistic calculations (i.e. where the studied objects have low relative velocities) the Coulomb gauge is practical to use. This gauge results from the condition

$$\nabla\mathbf{A} = 0 \tag{39}$$

which implies that λ obeys the Poisson equation:

$$\nabla^2\lambda = -\nabla\mathbf{A}. \tag{40}$$

The equations of motion are transformed to the following:

$$\Box\mathbf{A} = -\mu_0\mathbf{J} + \frac{1}{c^2}\nabla\dot{\phi} \tag{41}$$

$$\nabla^2\phi = -\rho/\epsilon_0. \tag{42}$$

Equation 42 has the following general solution:

$$\phi(\mathbf{r}, t) = \int \frac{\rho(\mathbf{r}', t)}{|\mathbf{r} - \mathbf{r}'|}\,\mathrm{d}\mathbf{r}' \tag{43}$$

So ϕ is just the instantaneous potential at some point in space, caused by the presence of a charge distribution ρ. In the following we will work with the Coulomb gauge.

[1] It might seem inconsistent to use the d'Alambertian on scalar fields and vector fields, but since the action of $\Box$ is unambiguously defined in both cases, the notation is clear.

2.3 Wave equations

In the absence of any charges, the potential ϕ and the current density $\mathbf{J}$ are zero everywhere. The equations of motion for the scalar and vector potential reduce to the the following:

$$\Box \mathbf{A} = \left[\nabla^2 - \frac{1}{c^2} \frac{\partial^2}{\partial t^2} \right] \mathbf{A} = 0. \tag{44}$$

This is called a *wave equation*. Since it is a second order differential equation, there are two linearly independent solutions, which are in this case given by:

$$\mathbf{A}(\mathbf{r}, t) = \mathbf{A}_0 \exp\{i(\mathbf{k} \cdot \mathbf{r} - \omega t)\} \tag{45}$$

Checking the validity of this solution yields the following:

$$\Box \mathbf{A}(\mathbf{r}, t) = \left[k^2 - \frac{\omega^2}{c^2} \right] \mathbf{A}(\mathbf{r}, t) = 0, \tag{46}$$

which implies that

$$k \stackrel{\text{def}}{=} |\mathbf{k}| = \pm \frac{\omega}{c}. \tag{47}$$

The vector $\mathbf{k}$ is called the *propagation vector*. A positive absolute value implies that the vector field moves forward, a negative absolute value implies a motion in the opposite direction. Since linear combinations of solutions are also solutions of the differential equation, it follows from Fourier theory that any function of the form $\mathbf{f}(\mathbf{k} \cdot \mathbf{r} - \omega t)$ is a solution to Eq. 44. From here on, we will look at forward moving waves. The electric and magnetic fields can be retrieved from $\mathbf{A}$ by Eqs. 26 and 28.

$$\begin{aligned} \mathbf{E}(\mathbf{r}, t) = -\dot{\mathbf{A}} &= i\omega \mathbf{A}_0 \exp\{i(\mathbf{k} \cdot \mathbf{r} - \omega t)\} \\ &:= \mathbf{E}_0 \exp\{i(\mathbf{k} \cdot \mathbf{r} - \omega t)\} \qquad (48) \\ \mathbf{B}(\mathbf{r}, t) = \nabla \times \mathbf{A} &= i[\mathbf{k} \times \mathbf{A}_0] \exp\{i(\mathbf{k} \cdot \mathbf{r} - \omega t)\} \\ &:= \mathbf{B}_0 \exp\{i(\mathbf{k} \cdot \mathbf{r} - \omega t)\}, \qquad (49) \end{aligned}$$

where Eq. 90 was used to derive Eq. 49. It follows from Eq. 49 that the magnetic field is perpendicular to the plane spanned by $\mathbf{k}$ and $\mathbf{A}_0$. The condition $\nabla \mathbf{E} = 0$ implies that $\mathbf{A}_0 \cdot \mathbf{k} = 0$. Since $\mathbf{E}_0$ is parallel to $\mathbf{A}_0$, it is clear that $\mathbf{E}$, $\mathbf{B}$ and $\mathbf{k}$ form a mutually orthogonal triad. It also follows that the electric and magnetic fields oscillate perpendicular to the propagation direction, indicated by $\mathbf{k}$. We now define the following:

$$\begin{aligned} \mathbf{k} &:= k\hat{\mathbf{k}} \qquad (50) \\ \mathbf{E}_0 &:= E_0 \hat{\mathbf{e}} \qquad (51) \\ \mathbf{B}_0 &:= B_0 \hat{\mathbf{b}} = B_0 (\hat{\mathbf{k}} \times \hat{\mathbf{e}}), \qquad (52) \end{aligned}$$

where $|\hat{\mathbf{k}}| = |\hat{\mathbf{e}}| = |\hat{\mathbf{b}}| = 1$. Equation 23*(d)* can then be written as:

$$\begin{aligned} \nabla \times \mathbf{E} &= -\dot{\mathbf{B}} \\ \nabla \times \mathbf{E}_0 \exp\{i(\mathbf{k}\cdot\mathbf{r} - \omega t)\} &= -\frac{\partial}{\partial t}\mathbf{B}_0 \exp\{i(\mathbf{k}\cdot\mathbf{r} - \omega t)\} \\ ikE_0[\hat{\mathbf{k}} \times \hat{\mathbf{e}}] &= i\omega B_o[\hat{\mathbf{k}} \times \hat{\mathbf{e}}]. \end{aligned}$$

it follows that:

$$B_0 = \frac{k}{\omega}E_0 = \frac{1}{c}E_0. \tag{53}$$

2.4 Poynting vector

The energy content of the electro magnetic field at a point in space and time is given by:

$$u(\mathbf{r}, t) = \frac{1}{2}\left[\mathbf{E}\cdot\mathbf{D} + \mathbf{B}\cdot\mathbf{H}\right]. \tag{54}$$

In order to study the change in energy content, carried by a traveling electro magnetic field, consider the time-derivative of u:

$$\begin{aligned} \dot{u} &= \frac{1}{2}[\dot{\mathbf{E}}\cdot\mathbf{D} + \mathbf{E}\cdot\dot{\mathbf{D}} + \dot{\mathbf{B}}\cdot\mathbf{H} + \mathbf{B}\cdot\dot{\mathbf{H}}] \\ &= \epsilon\mathbf{E}\cdot\dot{\mathbf{E}} + \frac{1}{\mu}\mathbf{B}\cdot\dot{\mathbf{B}} \\ &= \mathbf{E}\cdot\nabla\times\mathbf{H} - \mathbf{H}\cdot\nabla\times\mathbf{E} \\ &= \nabla(\mathbf{H}\times\mathbf{E}), \end{aligned} \tag{55}$$

where Eq. 91 was used in the last step. Integrating the energy-change over some volume in space gives the following:

$$\int_V \mathrm{d}v\ \dot{u} = \int_V \mathrm{d}v\ \nabla(\mathbf{H}\times\mathbf{E}) = -\oint_S \mathrm{d}s\ \mathbf{P}\cdot\hat{\mathbf{k}}, \tag{56}$$

where we used Gauss' theorem in the second step, and defined the *Poynting vector* $\mathbf{P}$:

$$\mathbf{P} = \mathbf{E}\times\mathbf{H}. \tag{57}$$

The interpretation of Eq. 56 is clear: the decrease of energy content in a volume V equals the energy flux normal to the surface S containing V (note that this can only be the direction of unit vector $\hat{\mathbf{k}}$). In a general description, both $\mathbf{E}$ and $\mathbf{H}$ can be complex. Since the electric and magnetic field are observable quantities, the convention is to take the real part of the complex functions $\mathbf{E}(\mathbf{r}, t)$ and $\mathbf{H}(\mathbf{r}, t)$. In a measurement, the oscillations will not be observed. The electro

magnetic field intensity I is defined as the cycle-averaged (time-averaged) value of the Poynting vector:

$$I = \frac{1}{\Delta t} \int_{t}^{t+\Delta t} \mathrm{Re}(\mathbf{E}) \times \mathrm{Re}(\mathbf{H}) \cdot \mathbf{n} \, \mathrm{d}t = \frac{1}{2}(\mathbf{E} \times \overline{\mathbf{H}}) \cdot \hat{\mathbf{k}}. \tag{58}$$

The quantity $\overline{\mathbf{H}}$ denotes the complex conjugate of $\mathbf{H}$. The last step is valid for any two complex quantities having a $\exp\{-i\omega t\}$-dependence. This is called the *cycle average theorem*, which is easy to prove by filling in the expressions for $\mathbf{E}$ and $\mathbf{H}$ and integrating over time. From Eq. 58 we obtain the following explicit formula:

$$\begin{aligned} I &= \frac{1}{2\mu_0}(\mathbf{E} \times \overline{\mathbf{B}}) \cdot \hat{\mathbf{k}} \\ &= \frac{1}{2\mu_0}(i\omega A_0) \cdot \overline{(ikA_0)} e^{i(\mathbf{k}\cdot\mathbf{r}-\omega)t} e^{-i(\mathbf{k}\cdot\mathbf{r}-\omega)t} (\hat{\mathbf{e}} \times [\hat{\mathbf{k}} \times \hat{\mathbf{e}}]) \cdot \hat{\mathbf{k}} \\ &= \frac{\omega k}{2\mu_0} A_0^2 \hat{\mathbf{k}} \cdot \hat{\mathbf{k}} = \frac{\epsilon_0 c^2 \omega k}{2} A_0^2 = \frac{1}{2} c \epsilon_0 \omega^2 A_0^2 = \frac{1}{2} c \epsilon_0 E_0^2 \end{aligned} \tag{59}$$

where $A_0 = |\mathbf{A}_0|$.

3 2-photon transitions

In perturbation theory, the interaction of a molecule with electro magnetic radiation is described by augmenting the molecular Hamiltonian H_0 with a radiation term coupling electrons to the electro magnetic field. The probability for 2-photon absorption is given by the second-order perturbation formula:

$$\mathcal{P}_{f \leftarrow i}(t) = |\langle f | U^{(2)}(t, t_0) | i \rangle|^2, \tag{60}$$

where $U^{(n)}$ is given by Eq. 19. This yields explicitly:

$$\begin{aligned} \langle f | U^{(2)} | i \rangle &= (-i\hbar)^{-2} \sum_m \int_{t_0}^{t} \int_{t_0}^{\tau_1} \mathrm{d}\tau_1 \mathrm{d}\tau_2 \; \langle f | U^{(0)}(t, \tau_1) V(\tau_2) U^{(0)}(\tau_1, \tau_2) | m \rangle \\ &\times \quad \langle m | V(\tau_1) U^{(0)}(\tau_2, t_0) | i \rangle \end{aligned} \tag{61}$$

If we disregard the magnetic coupling between electrons and the magnetic field, the potential operator $V(t)$ coupling the electrons to the electric field is given by:

$$\begin{aligned} V(t) &= -e\mathbf{E} \cdot \mathbf{r} = \tfrac{e}{2} \dot{\mathbf{A}}(\mathbf{r}, t) \\ &= -\tfrac{i}{2} e\omega A_0 \exp\{i(\mathbf{k} \cdot \mathbf{r} - \omega t)\} \hat{\mathbf{e}} \cdot \mathbf{r} \\ &\approx -\tfrac{i}{2} e\omega A_0 \exp\{-i\omega t\} \hat{\mathbf{e}} \cdot \mathbf{r} = V_0 \exp\{-i\omega t\}, \end{aligned} \tag{62}$$

where $\mathbf{r}$ represents all electronic coordinates, and the factor $1/2$ was inserted to ensure that $|\mathrm{Re}(\mathbf{E})| = |\mathbf{A}|$. The approximation $\mathbf{k} \cdot \mathbf{r} \approx 0$ is valid when the

molecular dimensions are smaller than the wavelength of the radiation. In a typical experiment wavelengths in the order of 10^2 nm are used, which justifies the assumption for small molecules. Plugging the potential into Eq. 61, and using Eq. 7 yields the following:

$$\langle f|U^{(2)}(t,t_0)|i\rangle = -\hbar^{-2}\sum_m \exp\{-i(\omega_f t)\}\exp\{i\omega_i t_0\}\langle f|V_0|m\rangle\langle m|V_0|i\rangle$$

$$\times \int_{t_0}^{t}\int_{t_0}^{\tau_1} \mathrm{d}\tau_1\mathrm{d}\tau_2 \;\exp\{i(\omega_f-\omega)\tau_1 + \epsilon\tau_1 - i(\tau_1-\tau_2)\omega_m - i(\omega_i+\omega)\tau_2 + \epsilon\tau_2\} \quad (63)$$

where the factor ϵ was introduced to converge the integral as t_0 approaches $-\infty$. At the end we let $\epsilon \to 0$. We also introduced the notation $\omega_x = E_x/\hbar$. The double integral can readily be worked out, this yields the following:

$$\begin{aligned}\langle f|U^{(2)}(t)|i\rangle &= \hbar^{-2}\sum_m \exp\{-i\omega_f t\}\exp\{i\omega_i t_0\}\langle f|V_0|m\rangle\langle m|V_0|i\rangle \\ &\times \frac{\exp\{(i\omega_f - i\omega - i\omega_i + 2\epsilon)t\}}{(\omega_m-\omega_i-\omega-i\epsilon)(\omega_f-2\omega-\omega_i-2i\epsilon)}. \end{aligned} \quad (64)$$

This yields for the transition probability:

$$\begin{aligned}\mathcal{P}(t) &= \hbar^{-4}\left|\sum_m \frac{\langle f|V_0|m\rangle\langle m|V_0|i\rangle}{\omega_i-\omega_m+\omega+i\epsilon/2}\right|^2 \times \left|\frac{\exp\{-i(2\omega-\omega_i+i\epsilon)t\}}{(\omega_i-\omega_f+2\omega+i\epsilon)}\right|^2 \\ &= \hbar^{-4}\left|\sum_m \frac{\langle f|V_0|m\rangle\langle m|V_0|i\rangle}{\omega_i-\omega_m+\omega+i\epsilon/2}\right|^2 \times \frac{\exp\{2\epsilon t\}}{(\omega_i-\omega_f+2\omega)^2+\epsilon^2}. \end{aligned} \quad (65)$$

For this expression, we used that $|\exp\{i\phi\}|^2 = 1$, and we let $\epsilon \to 2\epsilon$. The transition rate R is equal to the time-derivative of the absorption probability $\dot{\mathcal{P}}(t)$:

$$\dot{\mathcal{P}}(t) = \hbar^{-4}\left|\sum_m \frac{\langle f|V_0|m\rangle\langle m|V_0|i\rangle}{\omega_i-\omega_m+\omega+i\epsilon/2}\right|^2 \times \frac{2\epsilon\exp\{2\epsilon t\}}{(\omega_i-\omega_f+2\omega)^2+\epsilon^2} \quad (66)$$

for small ϵ, the numerator in the second term approaches 2ϵ. Letting $\epsilon \to 0$ yields a representation for the Dirac delta-function:

$$\lim_{\epsilon\to 0}\frac{2\epsilon}{x^2+\epsilon^2} = 2\pi\delta(x). \quad (67)$$

So we obtain:

$$R = 2\pi\hbar^{-4}\left|\sum_m \frac{\langle f|V_0|m\rangle\langle m|V_0|i\rangle}{\omega_i-\omega_m+\omega}\right|^2 \times \delta(\omega_i-\omega_f+2\omega) \quad (68)$$

From Eq. 62 we obtain the expression for V_0:

$$V_0 = -\tfrac{i}{2}e\omega A_0\hat{\mathbf{e}}\cdot\mathbf{r}. \quad (69)$$

plugging this into Eq. 68 yields the following:

$$\begin{aligned} R &= \frac{2\pi e^4\omega^4}{16\hbar^4}A_0^4\left|\sum_m \frac{\langle f|\hat{\mathbf{e}}\cdot\mathbf{r}|m\rangle\langle m|\hat{\mathbf{e}}\cdot\mathbf{r}|i\rangle}{\omega_i-\omega_m+\omega}\right|^2 \times \delta(\omega_i-\omega_f+2\omega) \\ &= \frac{\pi e^4}{2\epsilon_0^2c^2\hbar^4}I^2\left|\sum_m \frac{\langle f|\hat{\mathbf{e}}\cdot\mathbf{r}|m\rangle\langle m|\hat{\mathbf{e}}\cdot\mathbf{r}|i\rangle}{\omega_i-\omega_m+\omega}\right|^2 \times \delta(\omega_i-\omega_f+2\omega). \end{aligned} \tag{70}$$

Using the expression for the fine-structure constant α:

$$\alpha = \frac{1}{4\pi\epsilon_0}\frac{e^2}{\hbar c}, \tag{71}$$

we obtain the following for the transition rate:

$$R = (2\pi)^3\alpha^2\hbar^{-2}I^2\left|\sum_m \frac{\langle f|\hat{\mathbf{e}}\cdot\mathbf{r}|m\rangle\langle m|\hat{\mathbf{e}}\cdot\mathbf{r}|i\rangle}{\omega_i-\omega_m+\omega}\right|^2 \times \delta(\omega_i-\omega_f+2\omega). \tag{72}$$

We can check the units for this equation: since the quantity $\mathcal{P}$ should be dimensionless, R should have dimension s^{-1}. We will denote the unit of a quantity with square brackets, e.g. for mass M in grams we write $[M] = \mathrm{g}$. In the MKS unit system we have:

$$[\alpha] = 1 \tag{73}$$
$$[\hbar] = \mathrm{J}\cdot\mathrm{s} \tag{74}$$
$$[I] = \mathrm{J}/(\mathrm{cm}^2\mathrm{s}) \tag{75}$$
$$[\langle f|\hat{\mathbf{e}}\cdot\mathbf{r}|m\rangle] = \mathrm{cm} \tag{76}$$
$$[\omega] = \mathrm{s}^{-1} \tag{77}$$

The intensity is defined as the cycle-average of the Pointing vector, who's dimension is energy/area×time, so the dimension of I is the same. The dimension of the Dirac delta-function can be derived from it's definition (Eq. 67), and the notion that $[\epsilon] = t^{-1}$:

$$[\delta(\omega_i-\omega_f+2\omega)] = \frac{\mathrm{s}^{-1}}{\mathrm{s}^{-2}} = \mathrm{s}. \tag{78}$$

We thus find for $[R]$:

$$[R] = 1^3\cdot 1^2\cdot(\mathrm{Js})^{-2}\cdot(\mathrm{J}/(\mathrm{cm}^2\mathrm{s}))^2\cdot\left(\frac{\mathrm{cm}\cdot\mathrm{cm}}{\mathrm{s}^{-1}}\right)^2\cdot\mathrm{s} = \mathrm{s}^{-1} \tag{79}$$

The *two-photon generalized cross section* $\sigma^{(2)}$ is defined by:

$$R = \sigma^{(2)}\left(\frac{I}{\hbar\omega}\right)^2, \tag{80}$$

The units for the cross section become:

$$[\sigma] = \mathrm{s}^{-1} \left(\frac{\mathrm{J}}{\mathrm{J}/(\mathrm{cm}^2\mathrm{s})} \right)^2 = \mathrm{cm}^4 \cdot \mathrm{s} \tag{81}$$

The equation for the two-photon cross section now reads:

$$\sigma^{(2)}(\omega) = \frac{(2\pi)^3 \alpha^2 \omega^2}{e^4} \left| \sum\!\!\!\!\!\!\int_m \frac{\langle \psi_f | \hat{\mu} | \psi_m \rangle \langle \psi_m | \hat{\mu} | \psi_i \rangle}{\omega_i + \omega - \omega_m} \right|^2 \delta(\omega_i - \omega_f + 2\omega). \tag{82}$$

To compare the cross section with experiments, this formula can be treated in two ways. The first is to compute the *two-photon integrated line cross section* $I^{(2)}$:

$$\begin{aligned} I^{(2)}(f \leftarrow i) &= \int_{line} \mathrm{d}\omega \; \sigma^{(2)}(\omega) \\ &= \frac{(2\pi)^3 \alpha^2 \omega^2}{e^4} \left| \sum\!\!\!\!\!\!\int_m \frac{\langle \psi_f | \hat{\mu} | \psi_m \rangle \langle \psi_m | \hat{\mu} | \psi_i \rangle}{\omega_i + \omega - \omega_m} \right|^2 \end{aligned} \tag{83}$$

where the integration runs over the line width of the electro magnetic field, which is here assumed to be a block function. The unit $[I^{(2)}] = \mathrm{cm}^4$, and $\omega = \frac{1}{2}(\omega_f - \omega_i)$. This applies if the line width of the electro magnetic field is (much) larger than the bandwidth of the excited state. The second method can be used in the case where the bandwidth of the transition is larger than the line width of the electro magnetic field. The delta function is then replaced by it's original Lorentzian form:

$$\delta(\omega_i - \omega_f + 2\omega) \rightarrow \frac{1}{\pi} \frac{\epsilon}{(\omega_i - \omega_f + 2\omega)^2 + \epsilon^2}. \tag{84}$$

This is interpreted as the line width function for the excited state. In most cases we can set

$$\epsilon = 1/2\tau_R, \tag{85}$$

where τ_R is the radiative lifetime of the upper state. If the electro magnetic field is tuned to the maximum signal, we have once again $\omega = \frac{1}{2}(\omega_f - \omega_i)$, and we get for the cross section:

$$\sigma^{(2)} = \frac{(2\pi)^3 \alpha^2 \omega^2}{e^4} \left| \sum\!\!\!\!\!\!\int_m \frac{\langle \psi_f | \hat{\mu} | \psi_m \rangle \langle \psi_m | \hat{\mu} | \psi_i \rangle}{\omega_i + \omega - \omega_m} \right|^2 \frac{2\tau_R}{\pi} \tag{86}$$

which has units as in Eq. (81). Finally we note that for n-photon processes, the experimentally observed cross section can be enhanced by a factor $n!$, when a non-coherent electro magnetic field is used.

A Vector identities

$$\begin{aligned}
\nabla \cdot (\nabla \times \mathbf{A}) &= 0 && (87)\\
\nabla \times \nabla \phi &= 0 && (88)\\
\nabla \times (\nabla \mathbf{A}) &= \nabla(\nabla \cdot \mathbf{A}) - \nabla^2 \mathbf{A} && (89)\\
\nabla \times (\phi \mathbf{A}) &= (\nabla \cdot \phi)\mathbf{A} + \phi \nabla \times \mathbf{A} && (90)\\
\nabla \cdot (\mathbf{A} \times \mathbf{B}) &= \mathbf{B} \cdot \nabla \times \mathbf{A} - \mathbf{A} \cdot \nabla \times \mathbf{B} && (91)\\
\mathbf{A} \times \mathbf{B} &= -\mathbf{B} \times \mathbf{A} && (92)
\end{aligned}$$

B Units

Fundamental units in the atomic unit system. All quantities in the following table are dimensionless and equal 1.

Constant	Symbol
rest mass of the electron	m_e
elementary charge	e
Planck's constant divided by 2π	$\hbar = h/2\pi$
4π times the permittivity of free space	$4\pi\epsilon_0$

Here are some derived units:

Constant	Symbol	Recommended value (NIST)
length, Bohr	$a_0 = 4\pi\epsilon_0\hbar^2/m_e e^2$	0.529 177 2083(19) $\times 10^{-10}$ m
energy, Hartree	$E_h = \hbar^2/m_e a_0^2$	4.359 743 81(34) $\times 10^{-18}$ J
time	$\tau_0 = \hbar/E_h$	2.418 884 326 5 $\times 10^{-17}$ s
fine-structure constant	$1/4\pi\epsilon_0 \times e^2/\hbar c$	7.297 352 533(27)$\times 10^{-3}$
velocity of light	$c = \alpha^{-1}$	1.370 359 892$\times 10^{2}$ a.u.

Here are some conversion factors between the gaussian and the MKSA system:

Quantity	Gaussian	MKSA
Velocity of light	c	$(\mu_0\epsilon_0)^{-1/2}$
Electric field	$\mathbf{E}$	$\sqrt{4\pi\epsilon_0}\mathbf{E}$
Displacement	$\mathbf{D}$	$\sqrt{4\pi/\epsilon_0}\mathbf{D}$
Charge Density	ρ	$1/\sqrt{4\pi\epsilon_0}\rho$
Magnetic induction	$\mathbf{B}$	$\sqrt{4\pi/\mu_0}\mathbf{B}$
Magnetization	$\mathbf{M}$	$\sqrt{\mu_0/4\pi}\mathbf{M}$
Dielectric constant	ϵ	ϵ/ϵ_0
Permeability	μ	μ/μ_0

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