

3.4. Electron transitions induced by electromagnetic radiation

Except for very strong laser fields the interactions of the electrons with the external electromagnetic field may be treated as a perturbation.

The Fermi golden rule

Consider the first-order probability amplitude of the $i \rightarrow f$ transition

$$\begin{aligned} a^{(1)} &= -i \int_{t_0}^t dt' e^{i(E_f - E_i)t'} \langle f | V(t') | i \rangle \\ &= -i \int_{t_0}^t dt' e^{i\omega_{fi}t'} V_{fi}(t'), \end{aligned} \quad (1)$$

where ω_{fi} is the characteristic Bohr angular frequency of the transition, in atomic units $E_f - E_i$, while $V_{fi}(t')$ stand for the matrix element of the perturbation potential.

If we take a simple case, where the perturbation potential is constant between $t_0 = 0$ and t , and zero otherwise, the integral may be easily performed.

$$a^{(1)} = -\frac{V_{fi}}{\omega_{fi}} (e^{i\omega_{fi}t} - 1), \quad (2)$$

and obtain for the transition probability

$$w_{fi}(t) = |a^{(1)}|^2 = 2|V_{fi}|^2 \frac{1 - \cos \omega_{fi}t}{\omega_{fi}^2}. \quad (3)$$

The function

$$F(t, \omega_{fi}) = \frac{1 - \cos \omega_{fi}t}{\omega_{fi}^2} \quad (4)$$

has a sharp maximum around $\omega_{fi} = 0$ (with a peak value $t^2/2$ and $2\pi/t$ half-width). As a consequence the most probable transitions will be those with ω_{fi} not larger than $\delta\omega_{fi} = 2\pi/t$.

Let us investigate the transition probability as a function of time. If the energy in the transition is conserved, meaning $\omega_{fi} = 0$, then

$$w_{fi}(t) = |V_{fi}|^2 t^2. \quad (5)$$

If $\omega_{fi} \neq 0$ the transition probability will oscillate in time as the function $F(t, \omega_{fi})$. For time intervals longer than the $2\pi/\omega_{fi}$ period, the mean value of the function is $1/\omega_{fi}^2$, and the transition probability will oscillate around the mean value

$$\overline{w}_{fi} = \frac{2|V_{fi}|^2}{\omega_{fi}^2}. \quad (6)$$

Let us consider further the $(E_f - \epsilon, E_f + \epsilon)$ energy band around the final state energy, where the density of states

$$\rho_f(E) = \frac{N}{2\epsilon} \quad (7)$$

is considered to be constant, N being the number of the states in the band. The transition probability to a state f' from this band is obtained by the integral of (3)

$$\begin{aligned} w_{f'i}(t) &= 2 \int_{E_f - \epsilon}^{E_f + \epsilon} |V_{f'i}|^2 F(t, \omega_{f'i}) \rho_f(E) dE_{f'} \\ &= 2|V_{f'i}|^2 \rho_f(E) \int_{-\epsilon}^{+\epsilon} \frac{1 - \cos \omega_{f'i} t}{\omega_{f'i}^2} d\omega_{f'i}, \end{aligned} \quad (8)$$

where we have taken the matrix element $V_{f'i}$ to be constant in the considered energy interval. Further we assume the perturbation long enough for

$$\epsilon \gg 2\pi/t = \delta\omega_{f'i} = \delta E_f. \quad (9)$$

Because the function $F(t, \omega_{f'i})$ has important values only in the $\delta\omega_{f'i}$ interval, the integral over $(-\epsilon, +\epsilon)$ may be extended without significant error to infinity. On the other hand, only those transitions are probable, for which the energy is conserved within the $\delta E = 2\pi/t$ interval given by the uncertainty principle, so $E_f \approx E_i$. We obtain

$$\int_{-\epsilon}^{+\epsilon} \frac{1 - \cos \omega_{f'i} t}{\omega_{f'i}^2} d\omega_{f'i} \approx \int_{-\infty}^{+\infty} \frac{1 - \cos \omega_{f'i} t}{\omega_{f'i}^2} d\omega_{f'i} = \pi t. \quad (10)$$

The transition probability will be

$$w_{f'i}(t) = 2\pi |V_{f'i}|^2 \rho_f(E) t. \quad (11)$$

Thus we get for the transition probability per unit of time

$$W_{f'i} = \frac{dw_{f'i}(t)}{dt} = 2\pi |V_{f'i}|^2 \rho_f(E). \quad (12)$$

The formula above is called the Fermi golden rule. It was derived for a constant perturbation potential, but is valid also for any kind of electromagnetic perturbation.

The interaction between a charged particle and the electromagnetic radiation

The Hamiltonian of an electron in electromagnetic field may be written as

$$H = \frac{1}{2}(-i\nabla + \mathbf{A})^2 + V_S, \quad (13)$$

where \mathbf{A} is the vector potential, while V_S stands for the scalar potential. Applying to a wavefunction $\Psi(\mathbf{r}, t)$ we obtain

$$\begin{aligned} H\Psi &= \left[\frac{1}{2}(-i\nabla + \mathbf{A})^2 - V \right] \Psi \\ &= -\frac{1}{2}\nabla^2\Psi - \frac{i}{2}\nabla(\mathbf{A}\Psi) - \frac{i}{2}\mathbf{A}(\nabla\Psi) + \frac{\mathbf{A}^2}{2}\Psi + V_S\Psi. \end{aligned} \quad (14)$$

Using $\nabla\mathbf{A} = 0$, the second and third term will be the same. For electromagnetic fields of normal intensity we may neglect the term containing \mathbf{A}^2 . We separate the unperturbed Hamiltonian and the perturbation

$$H^0 = -\frac{1}{2}\nabla^2 + V_S \quad (15)$$

$$V(t) = -i\mathbf{A}\nabla. \quad (16)$$

The probability amplitude in first order will be

$$a^{(1)} = -\int_0^t dt' e^{i\omega_{fi}t'} \langle f | \mathbf{A}(\mathbf{r}, t') \nabla | i \rangle \quad (17)$$

If \mathbf{A} describes a wave packet, it may be written as a superposition of plain waves

$$\mathbf{A}(\mathbf{r}, t) = \int d\omega A_0(\omega) \hat{\epsilon} [e^{i(\mathbf{k}\mathbf{r} - \omega t + \delta_\omega)} + e^{-i(\mathbf{k}\mathbf{r} - \omega t + \delta_\omega)}]. \quad (18)$$

Here \mathbf{k} is the wave vector, $\hat{\epsilon}$ the polarization direction. The amplitude for a given plane wave with angular frequency ω may be written

$$\begin{aligned} a_\omega^{(1)} &= -A_0(\omega) [e^{i\delta_\omega} \langle f | e^{i\mathbf{k}\mathbf{r}} \hat{\epsilon} \nabla | i \rangle \int_0^t dt' e^{i(\omega_{fi} - \omega)t'} \\ &\quad + e^{-i\delta_\omega} \langle f | e^{-i\mathbf{k}\mathbf{r}} \hat{\epsilon} \nabla | i \rangle \int_0^t dt' e^{i(\omega_{fi} + \omega)t'}]. \end{aligned} \quad (19)$$

The integrals over time may be written analytically

$$\int_0^t dt' e^{i(\omega_{fi} - \omega)t'} = \frac{-i}{\omega_{fi} - \omega} [e^{i(\omega_{fi} - \omega)t} - 1] \quad (20)$$

$$\int_0^t dt' e^{i(\omega_{fi} + \omega)t'} = \frac{-i}{\omega_{fi} + \omega} [e^{i(\omega_{fi} + \omega)t} - 1]. \quad (21)$$

The length t of the pulse usually is much longer relative to the $2\pi/\omega$ period of the oscillation. The functions above for large values of t has sharp maxima for $\omega_{fi} = \omega$ and $\omega_{fi} = -\omega$. The first case corresponds to the absorption, while the second second case to the induced emission. The two equations express the Bohr frequency condition. Further we discuss separately the two terms, because if one has important values, the other is negligible.

In case of the absorption for a given angular frequency close to ω_{fi} the transition probability is

$$|a_\omega^{(1)}|^2 = 2A_0^2(\omega)|M_{fi}(\omega)|^2 F(t, \omega - \omega_{fi}). \quad (22)$$

Here we have use the already defined function

$$F(t, \Delta\omega_{fi}) = \frac{1 - \cos \Delta\omega_{fi}t}{\Delta\omega_{fi}^2} \quad (23)$$

with $\Delta\omega = \omega - \omega_{fi}$. We not the matrix element with

$$M_{fi}(\omega) = \langle f | e^{i\mathbf{k}\mathbf{r}} \hat{\epsilon} \nabla | i \rangle. \quad (24)$$

If the components with different frequencies of the wave packet are not coherent, the transition probability may be calculated as an integral over ω for the transition probabilities of the components.

Because $|a_\omega^{(1)}|^2$ has important values only in the small $\delta\omega$ vicinity of ω_{fi} (for the properties of function $F(t, \Delta\omega_{fi})$), we perform the integral only for this small interval

$$|a^{(1)}|^2 = 2 \int_{\delta\omega} d\omega A_0^2(\omega) |M_{fi}(\omega)|^2 F(t, \omega - \omega_{fi}). \quad (25)$$

A_0 and $M_{fi}(\omega)$ is taken constant in $\delta\omega$, and the integral of $F(t, \omega - \omega_{fi})$ may be extended to infinity

$$\int_{-\infty}^{+\infty} d\omega F(t, \omega - \omega_{fi}) = \pi t. \quad (26)$$

We obtain for the transition probability

$$|a^{(1)}|^2 = 2\pi A_0^2(\omega_{fi}) |M_{fi}(\omega_{fi})|^2 t. \quad (27)$$

The transition probability per unit of time will be

$$W_{fi} = 2\pi A_0^2(\omega_{fi}) |M_{fi}(\omega_{fi})|^2 \quad (28)$$

Further we derive the formula for the cross section of photon absorption In the formula for the cross section

$$\sigma_{i \rightarrow f} = \frac{N_{i \rightarrow f}}{J_Y N_X} \quad (29)$$

with $N_x = 1$ we multiply the nominator and the denominator by ω_{fi} , obtaining in the denominator the radiation intensity. This may be written in SI

$$I(\omega) = 2\varepsilon_0 \omega^2 c A_0^2(\omega), \quad (30)$$

or in atomic units

$$I(\omega) = \frac{1}{2\pi} \omega^2 c A_0^2(\omega). \quad (31)$$

The transition probability per unit of time may be written

$$W_{fi} = 4\pi^2 \frac{I(\omega_{fi})}{c\omega_{fi}^2} |M_{fi}(\omega_{fi})|^2. \quad (32)$$

The cross section

$$\sigma_{fi} = \frac{\omega_{fi} W_{fi}}{I(\omega_{fi})}. \quad (33)$$

In the nominator we have the absorbed energy per unit of time. Using (32) we obtain for the cross section

$$\sigma_{fi} = \frac{4\pi\alpha}{\omega_{fi}} |M_{fi}(\omega_{fi})|^2, \quad (34)$$

where we have introduced the fine structure constant $\alpha = 1/c = 1/137$.

Similarly we perform the calculations for the induced emission with $\omega_{fi} \approx -\omega$. The transition probabilities and cross sections are obtained the same

$$W_{if} = W_{fi} \quad (35)$$

$$\sigma_{if} = \sigma_{fi}. \quad (36)$$

We have to calculate the matrix element $M_{fi}(\omega_{fi})$ using (24). In many practical cases it is useful to perform the Taylor expansion

$$e^{i\mathbf{k}\mathbf{r}} = 1 + (i\mathbf{k}\mathbf{r}) + \frac{1}{2!}(i\mathbf{k}\mathbf{r})^2 + \dots \quad (37)$$

In the optical spectrum the wave number is of the order of magnitude $k = 2\pi/\lambda \sim 10^7 \text{ m}^{-1}$, while the atomic dimensions are around $r \sim 10^{-10} \text{ m}$. In these cases $\mathbf{k}\mathbf{r} \sim 10^{-3}$, and the $\exp(i\mathbf{k}\mathbf{r})$ may be approximated by 1. This is called the dipole approximation.

In dipole approximation

$$M_{fi} = \hat{\epsilon} \langle f | \nabla | i \rangle = i \hat{\epsilon} \langle f | \dot{\mathbf{r}} | i \rangle, \quad (38)$$

where we have used

$$-i\nabla = \dot{\mathbf{r}}. \quad (39)$$

The formula above is written in Coulomb or velocity gauge.

Sometimes it is useful to write the matrix element also in the length gauge. For this we use the Heisenberg-equation

$$\dot{\mathbf{r}} = -i[\mathbf{r}, H^0], \quad (40)$$

obtaining

$$\begin{aligned} \langle f | \dot{\mathbf{r}} | i \rangle &= -i \langle f | \mathbf{r} H^0 - H^0 \mathbf{r} | i \rangle \\ &= -i (E_i - E_f) \langle f | \mathbf{r} | i \rangle \\ &= i \omega_{fi} \mathbf{r}_{fi}. \end{aligned} \quad (41)$$

We may express the M_{fi} matrix element in terms of the matrix element of

$$M_{fi} = -\omega_{fi} \hat{\mathbf{e}} \mathbf{r}_{\mathbf{n}}. \quad (42)$$

The transition probability in dipole approximation will be

$$W_{fi} = 4\pi^2 \frac{I(\omega_{fi})}{c} |\hat{\mathbf{e}} \mathbf{r}_{\mathbf{n}}|^2. \quad (43)$$

The $\hat{\mathbf{e}} \mathbf{r}_{\mathbf{n}}$ scalar product may be written as $\mathbf{r}_{\mathbf{n}} \cos \theta$, where θ is the angle between \mathbf{r} and $\hat{\mathbf{e}}$. For isotropic non-polarized radiation the angle varies randomly. The transition probability for caused by the unpolarized radiation may be obtained by averaging over all possible angles

$$\frac{1}{4\pi} \int d\Omega \cos^2 \theta = \frac{1}{4\pi} \int_0^{2\pi} d\varphi \int_0^\pi \cos^2 \theta \sin \theta d\theta = \frac{1}{3}, \quad (44)$$

leading to

$$\overline{W}_{fi} = \frac{4\pi^2}{3} \frac{I(\omega_{fi})}{c} |\mathbf{r}_{\mathbf{n}}|^2. \quad (45)$$

The approximation above is called dipole, because the $\mathbf{r}_{\mathbf{n}}$ matrix elements are proportional to the matrix elements of the electric dipole

$$\mathbf{D}_{\mathbf{n}} = -\mathbf{r}_{\mathbf{n}}. \quad (46)$$