3. Time-dependent perturbation theory

We plan to investigate the electron transitions in atoms induced by an interaction with an external time-dependent potential (charged particles, electromagnetic waves etc.) We assume, that the interaction with the external field is not too large, and one can apply for the transition perturbation methods.

3.1. The basics of the method

We assume that the $H(t)$ time-dependent Hamiltonian of a quantummechanical system can be written as a sum of two terms

$$H(t) = H^0 + V(t). \tag{1}$$

Here H^0 does not depend on time, and its eigenstates and eigenvalues are known. $V(t)$ is a time-dependent perturbation (interaction), acting between t_0 and t.

Before t_0 the system is in an eigenstate of H^0, denoted by i. Due to the $V(t)$ perturbation it goes to another eigenstate, f. The evolution of the system between t_0 and t may be described by the $U(t,t_0)$ evolution operator. The wavefunction of the system at moment t will be

$$|\Psi\rangle = U(t,t_0)|i\rangle. \tag{2}$$

One may write for the evolution operator the differential equation

$$i\frac{\partial}{\partial t}U(t,t_0) = HU(t,t_0) \tag{3}$$

which is equivalent to the time-dependent Schrödinger-equation.

After the system has evolved to state $\Psi(t)$, and the perturbation stops acting, the system has to go to an eigenstate of the H^0. The probability of a transition to a certain state f depends on the $\langle f|\Psi\rangle$ overlap integral, which is called transition probability amplitude. The transition probability can be calculated as

$$w_{i\to f} = |\langle f|\Psi\rangle|^2 = |\langle f|U(t,t_0)|i\rangle|^2. \tag{4}$$

Further instead of the usual Schrödinger picture we use the interaction or the Dirac picture. In this case the time dependence of the $U_I(t,t_0)$ evolution operator contains only the influence of the perturbation, and does not contain the periodic factor present in the Schrödinger picture even for time-independent Hamiltonians

$$U_I(t,t_0) = U^{0\dagger}(t,t_0)U(t,t_0), \tag{5}$$

where $U^0(t,t_0)$ is the evolution operator of the system in the absence of the perturbation. The $U^0(t,t_0)$ satisfies the

$$i\frac{\partial}{\partial t}U^0(t,t_0) = H^0U^0(t,t_0) \tag{6}$$

differential equation, and the solution may be written as

$$U^0(t,t_0) = e^{-iH^0(t-t_0)}. \tag{7}$$

It can be proved that

$$i\frac{\partial}{\partial t}U_I(t,t_0) = V_I(t)U_I(t,t_0) \tag{8}$$

where

$$V_I(t) = U^{0\dagger}(t,t_0)V(t)U^0(t,t_0) \tag{9}$$

is the perturbation potential in the interaction picture. The eigenfunctions of H^0 in this interaction picture are identical to the stationary wavefunctions.

Integrating formally (8) between t_0 and t we obtain

$$U_I(t,t_0) = 1 - i\int_{t_0}^{t} dt_1 V_I(t_1)U_I(t_1,t_0), \tag{10}$$

1 is an integration constant obtained by the

$$U_I(t_0,t_0) = 1 \tag{11}$$

initial condition.

The (10) integral equation may be solved by the iteration method. Let's take as the first guess for the $U_I(t_1,t_0)$ evolution operator 1. In this 0th order approximation the perturbation interaction is neglected, the system remains unchanged. In the first order we get

$$U_I^1(t,t_0) = 1 - i\int_{t_0}^{t} dt_1 V_I(t_1) \tag{12}$$

For the second-order approximation we insert the operator obtained in first order into the right-hand side of (10)

$$U_I^2(t,t_0) = 1 - i\int_{t_0}^{t} dt_1 V_I(t_1) + (-i)^2\int_{t_0}^{t} dt_2 V_I(t_2)\int_{t_0}^{t_2} dt_1 V_I(t_1), \tag{13}$$

and so on. By this method we obtain the perturbation expansion of the evolution operator

$$U_I(t,t_0) = 1 + \sum_{n=1}^{\infty} U_I^{(n)}(t,t_0), \tag{14}$$

where $U_I^{(n)}$ is the nth order correction to the evolution operator. These corrections may be obtain by the integrals

$$\begin{aligned} U_I^{(n)} &= (-i)^n\int_{t_0}^{t} dt_n V_I(t_n)\int_{t_0}^{t_n} dt_{n-1} V_I(t_{n-1}) \\ &\quad \cdots\int_{t_0}^{t_3} dt_2 V_I(t_2)\int_{t_0}^{t_2} dt_1 V_I(t_1). \end{aligned} \tag{15}$$

We write the interactions using (9) into the Schrödinger picture

$$\begin{aligned} U_I^{(n)} &= (-i)^n \int_{t_0}^{t} dt_n U^{0\dagger}(t_n, t_0) V(t_n) U^0(t_n, t_0) \\ &\quad \times \int_{t_0}^{t_n} dt_{n-1} U^{0\dagger}(t_{n-1}, t_0) V(t_{n-1}) U^0(t_{n-1}, t_0) \cdots \\ \cdots &\quad \times \int_{t_0}^{t_3} dt_2 U^{0\dagger}(t_2, t_0) V(t_2) U^0(t_2, t_0) \\ &\quad \times \int_{t_0}^{t_2} dt_1 U^{0\dagger}(t_1, t_0) V(t_1) U^0(t_1, t_0). \end{aligned} \tag{16}$$

Writing the U^0 operators into the form (7), the moments t_0 reduce

$$\begin{aligned} U_I^{(n)} &= (-i)^n \int_{t_0}^{t} dt_n e^{iH^0 t_n} V(t_n) e^{-iH^0 t_n} \\ &\times \int_{t_0}^{t_n} dt_{n-1} e^{iH^0 t_{n-1}} V(t_{n-1}) e^{-iH^0 t_{n-1}} \ldots \\ &\times \int_{t_0}^{t_3} dt_2 e^{iH^0 t_2} V(t_2) e^{-iH^0 t_2} \int_{t_0}^{t_2} dt_1 e^{iH^0 t_1} V(t_1) e^{-iH^0 t_1}. \end{aligned} \tag{17}$$

The above expansion is equivalent to the Born series.

Let us write the transition amplitude in different approximations. The total amplitude is

$$a = \langle f | U_I(t, t_0) | i \rangle. \tag{18}$$

While the nth order amplitude

$$a^{(n)} = \langle f | U_I^{(n)}(t, t_0) | i \rangle. \tag{19}$$

In 0th order

$$a^{(0)} = \langle f | i \rangle = \delta_{if}, \tag{20}$$

because of the orthogonality of i and f we do not obtain transition.

Writing the first order amplitude we take into account that i and f are the eigenstates of H^0 with eigenvalues E_i and E_f

$$\begin{aligned} a^{(1)} &= -i \int_{t_0}^{t} dt_1 \langle f | e^{iH^0 t_1} V(t_1) e^{-iH^0 t_1} | i \rangle \\ &= -i \int_{t_0}^{t} dt_1 e^{i(E_f - E_i) t_1} \langle f | V(t_1) | i \rangle. \end{aligned} \tag{21}$$

The expression above means that the perturbation causes a transition in one step from the initial state to final state in moment t_1.

The second-order amplitude may be calculated as

$$a^{(2)} = -\int_{t_0}^{t} dt_2 \langle f | e^{iH^0 t_2} V(t_2) e^{-iH^0 t_2} \int_{t_0}^{t_2} dt_1 e^{iH^0 t_1} V(t_1) e^{-iH^0 t_1} | i \rangle. \tag{22}$$

Here taking into account the

$$\sum_k |k\rangle\langle k| = 1 \tag{23}$$

closure relation, the complete system of the eigenstates of H^0 is inserted into the expression, taking into account that the eigenvalues of H^0 are E_k

$$\begin{aligned} a^{(2)} &= -\int_{t_0}^{t} dt_2 \langle f|e^{iE_f t_2} V(t_2) e^{-iH^0 t_2} \\ &\quad \times \sum_k |k\rangle\langle k| \int_{t_0}^{t_2} dt_1 e^{iH^0 t_1} V(t_1) e^{-iE_i t_1} |i\rangle \\ &= -\sum_k \int_{t_0}^{t} dt_2 e^{i(E_f - E_k)t_2} \langle f|V(t_2)|k\rangle \\ &\quad \times \int_{t_0}^{t_2} dt_1 e^{i(E_k - E_i)t_1} \langle k|V(t_1)|i\rangle. \end{aligned} \tag{24}$$

Interpretation: the perturbation causes a transition in t_1 into the intermediate state k, and after that in moment t_2 causes another transition into the final state. Because intermediate states are not measured, we have to sum over all possible intermediate states (paths).

3.2. The cross section

A scattering process or an electron transition caused by a projectile can be characterized by the **cross section**.

Let's consider a scattering process, particles X being the target. This is bombarded by a monoenergetic beam of projectiles Y. J_Y – the flux of the projectiles, the number of the incident particles per unit of time and per unit of perpendicular area. We neglect the interaction between the projectiles.

First we take into account only elastic scattering. dN_Y is the number of scattered particles per unit of time in the direction Ω, element of solid angle $d\Omega$. This quantity may be written

$$dN_Y(\Omega) = J_Y \Sigma(\Omega) d\Omega. \tag{25}$$

where $\Sigma(\Omega)$ is a characteristic of the target. If we have in the target N_X identical scattering centers (target atoms), and we assume that there in no coherence between the scattered waves by different centers, and each projectile is scattered only once, the number of scattered particles will be proportional to the number of target atoms.

$$dN_Y(\Omega) = J_Y N_X \sigma_d(\Omega) d\Omega, \tag{26}$$

Here $\sigma_d(\Omega)$ is an area-like quantity, and is a characteristic of one scattering center. This is the elastic differential cross section. We introduce σ_e, the total differential cross section

$$\sigma_d \equiv \frac{d\sigma_e}{d\Omega} = \frac{dN_Y(\Omega)}{J_Y N_X d\Omega}. \tag{27}$$

and

$$\sigma_e = \int \sigma_d(\Omega) d\Omega. \tag{28}$$

This quantity is approximately equal to the area of a circle with the radius being the range of the potential between the two particles.

In the case of an inelastic collision the target quantum state is changed, from i to f. The characteristic cross section for this transition may be written

$$\sigma_{i\to f} = \frac{N_{i\to f}}{J_Y N_X}. \tag{29}$$

We also may define several differential cross sections. For example

$$\frac{d^{2n-1}\sigma_{i\to f}}{d\Omega_1 \cdots d\Omega_n dE_1 \cdots dE_{n-1}}. \tag{30}$$

Further we assume, that we have only one scattering center, which is bombarded by a monoenergetic beam of identical particles. The quantum state of the projectiles differ only in the impact parameter relative to the target.

Let $w(i, \Phi_{\mathbf{b}} \to f)$ be the probability of the transition $i \to f$ for impact parameter $\mathbf{b}$-t. If in the unit of time are scattered N_Y particles, the number of $i \to f$ transitions are

$$N_{i\to f} = \sum_{j=1}^{N_Y} w(i, \Phi_{\mathbf{b_j}} \to f) \tag{31}$$

If $N_Y \to \infty$, the sum is transformed into an integral over a perpendicular plane to the beam direction

$$N_{i\to f} = \int d^2\mathbf{b} J_Y w(i, \Phi_{\mathbf{b}} \to f). \tag{32}$$

We assume a homogeneous flux

$$N_{i\to f} = J_Y \int d^2\mathbf{b} w(i, \Phi_{\mathbf{b}} \to f). \tag{33}$$

Comparing (33) with (29) and taking into account that $N_X = 1$, for the cross section we obtain

$$\sigma_{i\to f} = \int d^2\mathbf{b} w(i, \Phi_{\mathbf{b}} \to f). \tag{34}$$

We will use this formula for further calculations. Similarly, the (30) differential cross section may be expressed

$$\frac{d^{2n-1}\sigma_{i\to f}}{d\Omega_1 \cdots d\Omega_n dE_1 \cdots dE_{n-1}} = \int d^2\mathbf{b} w(i, \Phi_{\mathbf{b}} \to f, \Phi'), \tag{35}$$

where $|\Phi'\rangle$ is the final state with a given energy and angular distribution.

3.3. Electron transitions induced by charged particles

If the projectile has large energy, it may be described classically. For this approximation to be valid the de Broglie wavelength of the projectile should be much less relative to the atomic dimensions. If also the energy and momentum transfer are negligible to the projectile energy and momentum

$$p_i \approx p_f >> \sqrt{2M\Delta E}, \tag{36}$$

(p_i and p_f being the initial and final momentum, M the mass of the projectile, ΔE the energy transfer), the movement of the projectile is approximated by a straight-line trajectory and constant velocity. This approximation is called semiclassical approximation (SCA) or impact parameter method (IPM)

Taking into account (4) and (34) the cross section for transition $i \to f$ may be obtained

$$\begin{aligned} \sigma_{i\to f} &= \int d^2\mathbf{b}|a_{i\to f}(b)|^2 \\ &= \int d^2\mathbf{b}|\langle f|U_{\mathbf{b}}(+\infty,-\infty)|i\rangle|^2. \end{aligned} \tag{37}$$

Quantum states i and f, and the $U_{\mathbf{b}}(+\infty,-\infty)$ evolution operator are for the electron system. The projectile-electron interaction is taken to be the perturbation.

One-electron transitions

We assume the independent-electron approximation, and take into account only one active electron. If the energy of the projectile is much larger relative to the interaction, we may apply first-order perturbation theory. Usually this is valid for projectiles above 100 keV/u$\times Z_p^2$ energy, Z_p being the charge of the projectile.

Let us take an excitation process. The amplitude in first order may be calculated from (21). The perturbation potential is the Coulomb-interaction between the projectile and the active electron

$$V(t) = \frac{-Z_p}{R_{pe}(t)} = -\frac{Z_p}{|\mathbf{R}(t)-\mathbf{r}|}, \tag{38}$$

R_{pe} being the distance between the projectile and the electron, $\mathbf{R}$ and $\mathbf{r}$ the position vectors of the projectiles and the active electron, respectively. Taking the origin in the nucleus, we can write

$$\mathbf{R} = \mathbf{b}+\mathbf{z} \tag{39}$$

$$R = \sqrt{b^2+z^2}. \tag{40}$$

We change the variable in the time integral from (21)

$$z = vt; \qquad dz = vdt, \tag{41}$$

and we obtain for the first-order amplitude

$$a^{(1)} = i\frac{Z_p}{v}\int_{-\infty}^{+\infty} dz e^{i\frac{E_f - E_i}{v}z}\langle f|\frac{1}{|\mathbf{R}(t) - \mathbf{r}|}|i\rangle. \tag{42}$$

The potential is expanded into the multipole series

$$\frac{1}{|\mathbf{R}(t) - \mathbf{r}|} = \sum_{l=0}^{\infty}\frac{4\pi}{2l+1}\frac{r_<^l}{r_>^{l+1}}\sum_{m=-l}^{l} Y_{lm}^*(\hat{\mathbf{R}})Y_{lm}(\hat{\mathbf{r}}), \tag{43}$$

and we separate the orbital part of the electron wavefunctions

$$\begin{aligned} i &= R_i(r)Y_{l_i m_i}(\hat{\mathbf{r}}) & (44)\\ f &= R_f(r)Y_{l_f m_f}(\hat{\mathbf{r}}). & (45)\end{aligned}$$

Using the analytical formula for the integration of the product of three spherical harmonics, we obtain

$$\begin{aligned} a^{(1)} &= i\frac{Z_p}{v}\sum_l \frac{4\pi}{2l+1}\sqrt{\frac{(2l_i+1)(2l+1)}{4\pi(2l_f+1)}}C_{l_i 0 l 0}^{l_f 0} \\ &\times \sum_m C_{l_i m_i l m}^{l_f m_f}\int_{-\infty}^{+\infty} dz e^{i\frac{E_f - E_i}{v}z} Y_{lm}^*(\hat{\mathbf{R}}) \\ &\times \int_0^{\infty} r^2 dr R_f^*(r)\frac{r_<^l}{r_>^{l+1}}R_i(r). \end{aligned} \tag{46}$$

Let us look now to the ionization process. The ejected electron may leave the atom with different energies and angular momenta. It is usual to expand the final state into a series of the eigenstates of L^2 and L_z (spherical harmonics)

$$\psi_{\mathbf{p}}(\mathbf{r}) = \sum_{l_f} i^{l_f}e^{i\delta_{l_f}}R_{l_f}(pr)\sum_{m_f} Y_{l_f m_f}^*(\hat{\mathbf{p}})Y_{l_f m_f}(\hat{\mathbf{r}}). \tag{47}$$

This expansion is called the partial-wave expansion of the ejected electron, δ_{l_f} being the phaseshift, $\mathbf{p}$ the momentum of the electron $R_{l_f}(pr)$ the radial function of the partial wave. For plane waves (no interaction) the partial waves are the spherical Bessel functions, for purely Coulomb potential may be expressed by the Coulomb waves

$$R_{l_f}(pr) = \sqrt{\frac{2}{\pi}}\frac{1}{pr}F_{l_f}(-\frac{Z}{p}, pr), \tag{48}$$

while in other cases has to be obtained numerically (by solving the radial Schrödinger equation.

Using the same method as for the excitation we can obtain the amplitude

$$\begin{aligned} a^{(1)}_{l_f m_f}(\mathbf{p}) &= i^{l_f+1} e^{i\delta_{l_f}} \frac{Z_p}{v} \sum_l \frac{4\pi}{2l+1} \sqrt{\frac{(2l_i+1)(2l+1)}{4\pi(2l_f+1)}} C^{l_f 0}_{l_i 0 l 0} \\ &\times \sum_m C^{l_f m_f}_{l_i m_i l m} Y^*_{l_f m_f}(\hat{\mathbf{p}}) \int_{-\infty}^{+\infty} dz e^{i \frac{E_f - E_i}{v} z} Y^*_{lm}(\hat{\mathbf{R}}) \\ &\times \int_0^\infty r^2 dr R^*_{l_f}(pr) \frac{r^l_<}{r^{l+1}_>} R_i(r), \end{aligned} \tag{49}$$

and the differential cross section in terms of the direction and magnitude of the final momentum of the electron

$$\frac{d^2\sigma}{d\hat{\mathbf{p}}dp} = \int d^2\mathbf{b} | \sum_{l_f m_f} a^{(1)}_{l_f m_f}(\mathbf{p})|^2. \tag{50}$$

If we need the total cross section we have to integrate over the momentum vector. Using the orthonormality of the $Y^*_{l_f m_f}(\hat{\mathbf{p}})$ spherical harmonics, integration over the angles is easily performed, and we get

$$\sigma = \int d^2\mathbf{b} \int_0^\infty p^2 dp \sum_{l_f m_f} |a^{(1)}_{l_f m_f}(p)|^2, \tag{51}$$

where the amplitude does not contain the $Y^*_{l_f m_f}(\hat{\mathbf{p}})$ functions, and does not depend on the direction of the momentum. The energy of the final state may be written as

$$E_f = E^+_f + \frac{p^2}{2}, \tag{52}$$

or

$$E_f - E_i = I + \frac{p^2}{2}, \tag{53}$$

where$I$ is the ionization potential.