Electron transitions

Time-dependent perturbation theory

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

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

The solution may be written

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

It can be proved that

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

where

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

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

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

1 is an integration constant obtained by the

$$U_I(t_0, t_0) = 1 \quad (11)$$

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

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

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

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

- **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).