

Lecture

Second-Order Transitions

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Reading:

Brennan Chapter 4.5

Fermi's golden rule for first-order transitions

Recall the transition rate of **first-order transition** is expressed by Fermi's golden rule:

$$W = \frac{2\pi}{\hbar} \left| \langle k|V|s \rangle \right|^2 \rho_f(E_s) \quad (\text{there is a band of energy for the final states});$$

$$\text{Or: } W = \frac{2\pi}{\hbar} \left| \langle k|V|s \rangle \right|^2 \delta(E_k - E_s) \quad (\text{single state transition; energy conserved})$$

Where s is the initial state, k is the final state, V is the time-dependent perturbation, $\rho_f(E_s)$ describes the final density-of-states.

Therefore, transition rate W depends on two terms:

$\left| \langle k|V|s \rangle \right|^2$: *the coupling between the initial and the final states;*

$\rho_f(E_s)$: *final density-of-states.*

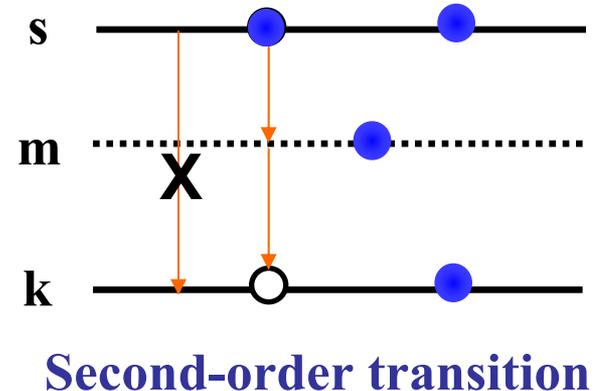
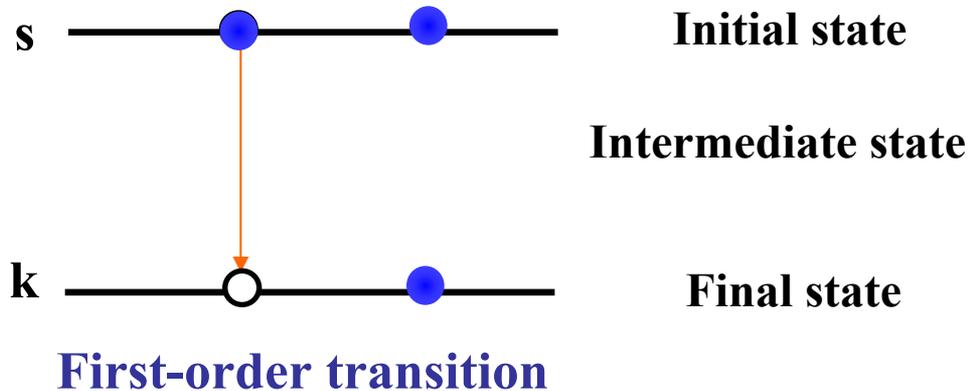
Forbidden transitions: If matrix elements of $\langle k|V|s \rangle$ vanishes, the transition between the initial and the final states cannot occur.

Examples:

1. Some transitions between excited atomic states;
2. Optical transitions in certain semiconductors.

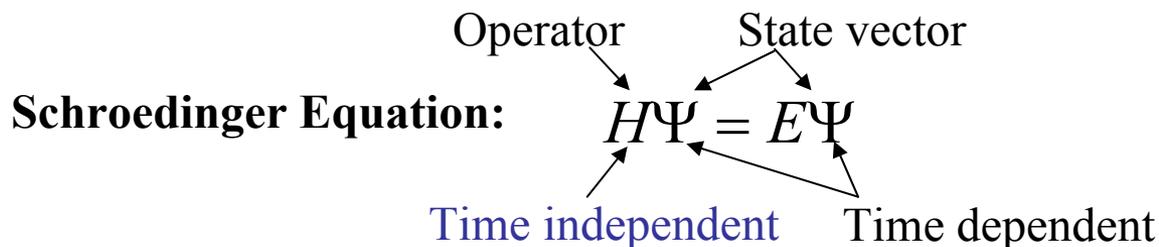
Second-order transitions

- Forbidden transitions cannot occur to first order, but they may occur to second and higher order through some intermediate path.
- For example, a transition can occur first from initial state s to an intermediate state m followed by decay to the final state k .
- The net result of a second-order transition is the same as in a direct transition but the path is different.



Different formalism pictures in Quantum Mechanics

- To understand how second or higher order transitions occur and to derive the transition rate, a different but equivalent formalism can be used, which is called the **interaction picture**.
- In the interaction picture both the state vectors and the operators exhibit time dependence.
- The interaction picture is intermediate between the Schroedinger and the Heisenberg pictures.



	Schroedinger Picture	Heisenberg Picture	Interaction Picture
State vectors	Time dependent	Time independent	Time dependent
Operators	Time independent	Time dependent	Time dependent

Equivalent Schroedinger equation in the interaction picture

How to write the Schroedinger equation in the interaction picture?

In Schroedinger picture, in the presence of some perturbation V the Schroedinger equation can be written as:

$$(H_0 + V)\Psi(t) = i\hbar \frac{d\Psi(t)}{dt}$$

Define a state vector $\Psi'(t)$ that is the time-evolved form of $\Psi(t)$ as:

$$\Psi'(t) \equiv e^{\frac{iH_0 t}{\hbar}} \Psi(t)$$

Take the differentiation of the above definition, we can construct the equation of the motion for $\Psi'(t)$:

$$\frac{d\Psi'}{dt} = \frac{iH_0}{\hbar} e^{\frac{iH_0 t}{\hbar}} \Psi(t) + e^{\frac{iH_0 t}{\hbar}} \frac{d\Psi(t)}{dt}$$

Both sides of the above equation are multiplied by $i\hbar$,

$$i\hbar \frac{d\Psi'}{dt} = -H_0 e^{\frac{iH_0 t}{\hbar}} \Psi(t) + e^{\frac{iH_0 t}{\hbar}} i\hbar \frac{d\Psi(t)}{dt}$$

Equivalent Schroedinger equation in the interaction picture

Cont'd:

$$i\hbar \frac{d\Psi'}{dt} = -H_0 e^{\frac{iH_0 t}{\hbar}} \Psi(t) + e^{\frac{iH_0 t}{\hbar}} i\hbar \frac{d\Psi(t)}{dt}$$

Insert the expression of Schroedinger equation into the second term at the right side of the above equation,

$$i\hbar \frac{d\Psi'}{dt} = -H_0 e^{\frac{iH_0 t}{\hbar}} \Psi(t) + e^{\frac{iH_0 t}{\hbar}} (H_0 + V) \Psi(t) = e^{\frac{iH_0 t}{\hbar}} V \Psi(t)$$

And from the definition: $\Psi(t) \equiv e^{-\frac{iH_0 t}{\hbar}} \Psi'(t)$

Therefore $i\hbar \frac{d\Psi'}{dt} = e^{\frac{iH_0 t}{\hbar}} V e^{-\frac{iH_0 t}{\hbar}} \Psi'(t)$

Define V' as: $V' \equiv e^{\frac{iH_0 t}{\hbar}} V e^{-\frac{iH_0 t}{\hbar}}$

Then we got the **equivalent Schroedinger equation** in the **interaction picture**:

$$i\hbar \frac{d\Psi'(t)}{dt} = V' \Psi'(t)$$

The operator V' can be thought of as an effective Hamiltonian, which is **time dependent**.

Time dependence of operator V' is determined by H_0 . Time dependence of state vector ψ is determined by the perturbation.

Time-evolution operators in Schroedinger and interaction pictures

In the Schroedinger picture a linear operator $T(t, t_0)$ is defined as a time-translation or time-evolution operator, which is used to derive the transition rate for first-order transitions.

$T(t, t_0)$ translates the system in time from $t = t_0$ to $t = t$, which is quantitatively defined as:

Schroedinger picture $\Psi(t) = T(t, t_0)\Psi(t_0)$

In the interaction picture, a time-evolution operator $U(t, t_0)$ is similarly defined, which can be used for the derivation of the transition rate for second and higher order transitions.

Interaction picture $\Psi'(t) = U(t, t_0)\Psi'(t_0)$

If $U(t, t_0)$ can be solved, then the transition probability and rate between the initial state $\Psi(t_0)$ and the final state can be calculated.

Time-evolution operators in Schroedinger and interaction pictures

What is the relationship between $T(t, t_0)$ and $U(t, t_0)$?

As defined previously, in interaction picture:

$$\Psi'(t) = U(t, t_0) \Psi'(t_0)$$

Insert the definition of $\Psi'(t)$:

$$\Psi'(t) \equiv e^{\frac{iH_0 t}{\hbar}} \Psi(t)$$



$$e^{\frac{iH_0 t}{\hbar}} \Psi(t) = U(t, t_0) e^{\frac{iH_0 t_0}{\hbar}} \Psi(t_0)$$

Times $e^{-\frac{iH_0 t}{\hbar}}$ at both the left and right sides:



$$\Psi(t) = e^{-\frac{iH_0 t}{\hbar}} U(t, t_0) e^{\frac{iH_0 t_0}{\hbar}} \Psi(t_0)$$

From the definition of $T(t, t_0)$:

$$\Psi(t) = T(t, t_0) \Psi(t_0)$$

Then we got:

$$U(t, t_0) = e^{\frac{iH_0 t}{\hbar}} T(t, t_0) e^{-\frac{iH_0 t_0}{\hbar}}$$

Solution of time-evolution operator $U(t, t_0)$ in interaction picture

To solve $U(t, t_0)$ in the interaction picture, first let us see how $T(t, t_0)$ is solved in the Schrodinger picture.

The time-translation operator $T(t, t_0)$ can be determined with the help from the time-dependent Schrodinger equation, which is:

$$i\hbar \frac{d\Psi(t)}{dt} = H(t)\Psi(t) \implies \frac{d\Psi(t)}{\Psi(t)} = \frac{-iH(t)}{\hbar} dt$$

Integrating with respect to time, we can write the above equation as:

$$\int_{\Psi(t_0)}^{\Psi(t)} \frac{d\Psi(t)}{\Psi(t)} = \frac{-i}{\hbar} \int_{t_0}^t H dt$$

Integrating and substituting in the bounds on the left-hand side yields, if H is time independent,

$$\ln \left[\frac{\Psi(t)}{\Psi(t_0)} \right] = -iH \frac{(t-t_0)}{\hbar}$$

Which reduces to: $\Psi(t) = \Psi(t_0) e^{\frac{-iH(t-t_0)}{\hbar}}$ } $\implies T(t, t_0) = e^{\frac{-iH(t-t_0)}{\hbar}}$

Definition of $T(t, t_0)$: $\Psi(t) = T(t, t_0)\Psi(t_0)$

Solution of time-evolution operator $U(t, t_0)$ in interaction picture

Cont'd:

$$T(t, t_0) = e^{\frac{-iH(t-t_0)}{\hbar}}$$

For small time increments $(t-t_0) \sim \varepsilon$ operator $T(t, t_0)$ can be expressed by a Taylor series expansion of the exponent as:

$$T(t + \varepsilon, t) = 1 - \frac{iH\varepsilon}{\hbar}$$

Because $T(t, t_0)$ is a linear operator:

$$T(t + \varepsilon, t_0) = T(t + \varepsilon, t)T(t, t_0)$$

The derivative $T(t, t_0)$ can be evaluated as:

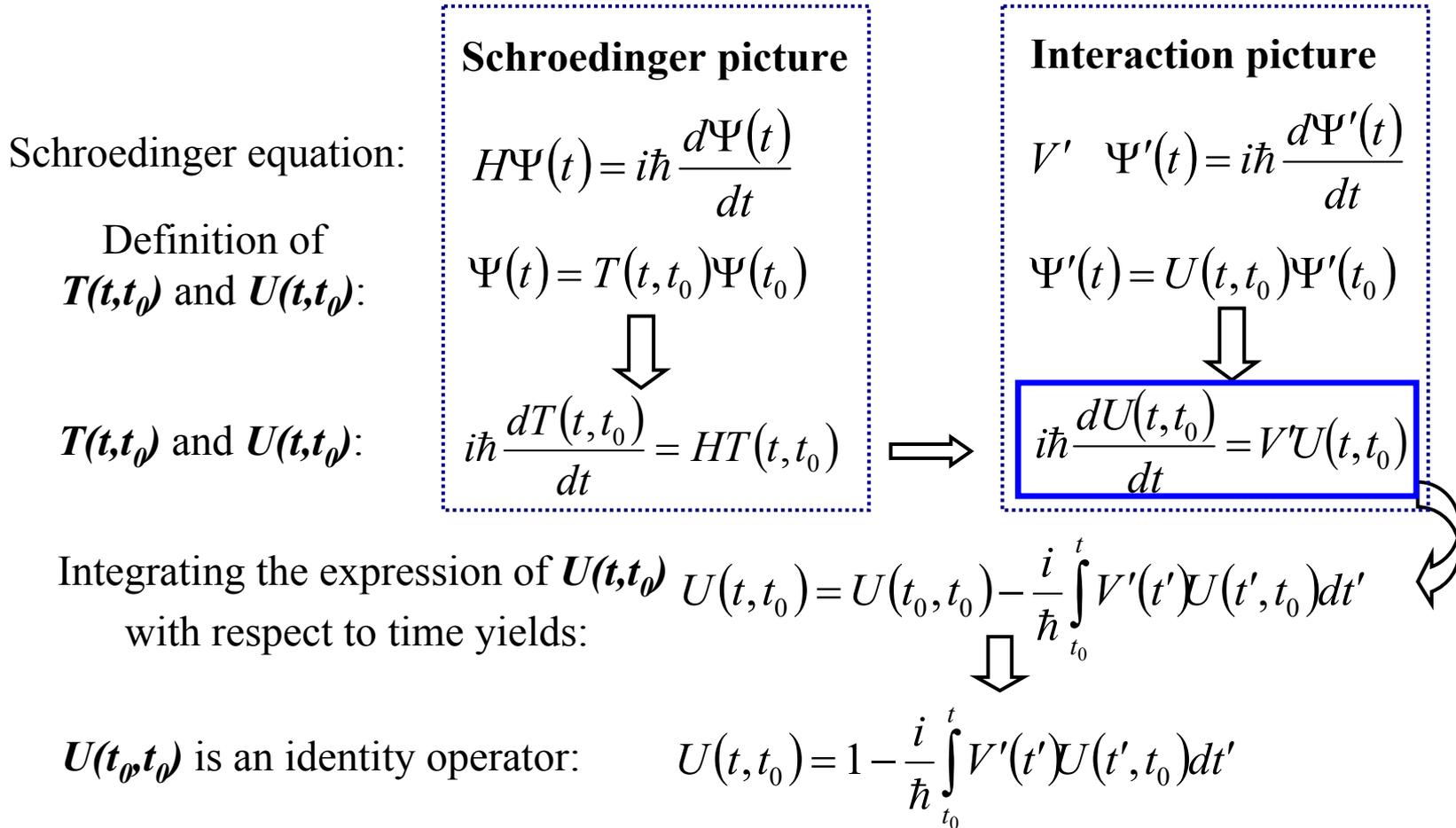
$$\begin{aligned} \frac{dT(t, t_0)}{dt} &= \lim_{\varepsilon \rightarrow 0} \frac{T(t + \varepsilon, t_0) - T(t, t_0)}{\varepsilon} \\ &= \lim_{\varepsilon \rightarrow 0} \frac{[T(t + \varepsilon, t) - 1]T(t, t_0)}{\varepsilon} \\ &= -\frac{i}{\hbar} HT(t, t_0) \end{aligned}$$

Then we get:

$$i\hbar \frac{dT(t, t_0)}{dt} = HT(t, t_0)$$

Solution of time-evolution operator $U(t, t_0)$ in interaction picture

From the similarity of the Schroedinger picture and interaction picture, we can get the expression for $U(t, t_0)$ based on the result of $T(t, t_0)$ obtained previously:



Solution of time-evolution operator $U(t, t_0)$ in interaction picture

Cont'd:

$$U(t, t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^t V'(t') U(t', t_0) dt'$$

This integral equation can be approximately solved as following using an iterative procedure if the perturbation is small.

First the value of $U(t', t_0)$ is approximated by $U = 1$. Substituting it into the above integral equation we get the zeroth-order value for $U(t, t_0)$:

$$U(t, t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^t V'(t') dt'$$

Substituting this zeroth-order $U(t, t_0)$ into the integral equation again we get the first-order value of $U(t, t_0)$

$$U(t, t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^t V'(t') \left(1 - \frac{i}{\hbar} \int_{t_0}^{t'} V'(t'') dt'' \right) dt' = 1 - \frac{i}{\hbar} \int_{t_0}^t V'(t') dt' + \left(-\frac{i}{\hbar} \right)^2 \int_{t_0}^t V'(t') dt' \int_{t_0}^{t'} V'(t'') dt''$$

By repeating this procedure we get higher orders of solution until the level of accuracy is obtained. The iterative solution can be written as:

$$U(t, t_0) = 1 - \frac{i}{\hbar} \int_{t_0}^t V'(t') dt' + \left(-\frac{i}{\hbar} \right)^2 \int_{t_0}^t V'(t') dt' \int_{t_0}^{t'} V'(t'') dt'' + \dots$$

Probability of transition between the initial and final states

The probability amplitude of the electron will be found in a final state k at a later time t is given by the k th coefficient C_k , which is determined from the overlap of the state Ψ_k on the state $\Psi'(t)$ as:

$$C_k = \int \Psi_k^* \Psi'(t) d^3r$$

$\Psi'(t)$ can be written as $U(t, t_0)\Psi_s$, assuming the system is in state s initially. Therefore C_k can be expressed in Dirac notation as:

$$C_k = \langle k | U(t, t_0) | s \rangle$$

Substituting the expansion for $U(t, t_0)$ into the above expression yields:

$$C_k = \underbrace{-\frac{i}{\hbar} \int_{t_0}^t \langle k | V' | s \rangle dt'}_{\substack{\text{first-order transition} \\ \text{probability amplitude}}} + \underbrace{\left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^t dt' \int_{t_0}^{t'} \langle k | V'(t') V'(t'') | s \rangle dt''}_{\substack{\text{second-order transition} \\ \text{probability amplitude}}} + \dots$$

Insert $V' \equiv e^{\frac{iH_0 t}{\hbar}} V e^{-\frac{iH_0 t}{\hbar}}$ and rewrite the second term as:

$$C_k(t) = \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' \sum_m \left\langle k \left| e^{\frac{iH_0 t}{\hbar}} V e^{-\frac{iH_0 t}{\hbar}} \right| m \right\rangle \left\langle m \left| e^{\frac{iH_0 t}{\hbar}} V e^{-\frac{iH_0 t}{\hbar}} \right| s \right\rangle$$

Probability and rate of second-order transition

Cont'd

$$C_k(t) = \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' \sum_m \left\langle k \left| e^{\frac{iH_0 t'}{\hbar}} V e^{-\frac{iH_0 t''}{\hbar}} \right| m \right\rangle \left\langle m \left| e^{\frac{iH_0 t}{\hbar}} V e^{-\frac{iH_0 t}{\hbar}} \right| s \right\rangle$$

Using the property of exponential operators ($\Psi_l^{(0)}$ is an arbitrary definite eigenstate):

$$e^{\frac{iH_0 t}{\hbar}} \Psi_l^{(0)} = e^{\frac{iE_l^{(0)} t}{\hbar}} \Psi_l^{(0)}$$

The second-order C_k can be rewritten as:

$$C_k(t) = \left(-\frac{i}{\hbar}\right)^2 \int_{t_0}^t dt' \int_{t_0}^{t'} dt'' \sum_m \langle k|V|m\rangle \langle m|V|s\rangle e^{\frac{i(E_k - E_m)t'}{\hbar}} e^{\frac{i(E_m - E_s)t''}{\hbar}} e^{\eta(t'+t'')}$$

where $e^{\eta(t'+t'')}$ is added to model a slow turn on of the potential. The fact η approaches 0 in the limit.

If we take t_0 to approach $-\infty$, let η approach 0 in the limit, and perform the integrations over t' and t'' , square, and take the time derivative, we can write the second-order transition rate as:

$$W_{s \rightarrow k} = \frac{2\pi}{\hbar} \left| \sum_m \frac{\langle k|V|m\rangle \langle m|V|s\rangle}{E_s - E_m} \right|^2 \delta(E_k - E_s)$$

Probability and rate of second-order transition

In summary, the transition rate for second-order transition is derived by the following path:

$$T(t, t_0) \longrightarrow U(t, t_0) \longrightarrow C_k(t) \longrightarrow W_{s \rightarrow k}$$

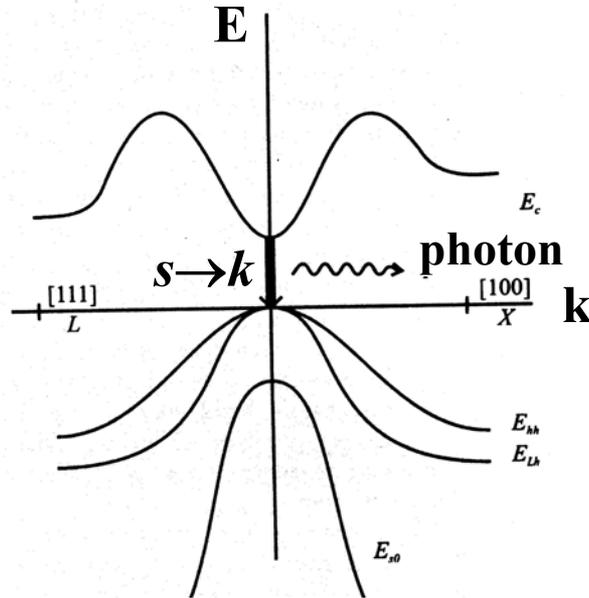
$$W_{s \rightarrow k} = \frac{2\pi}{\hbar} \left| \sum_m \frac{\langle k|V|m\rangle \langle m|V|s\rangle}{E_s - E_m} \right|^2 \delta(E_k - E_s)$$

Several issues on second-order transition:

1. The transition probability is proportional to the product of two separate transition ($s \rightarrow m$ and $m \rightarrow k$) probabilities or matrix elements. Therefore the probability is far less than that for a first order transition since it involves the product of two probabilities.
2. To determine the overall transition rate we must sum over the complete set of all intermediate states m before squaring.
3. The intermediate states need not be real. The system can make a transition to an intermediate virtual state and then to a final real state.

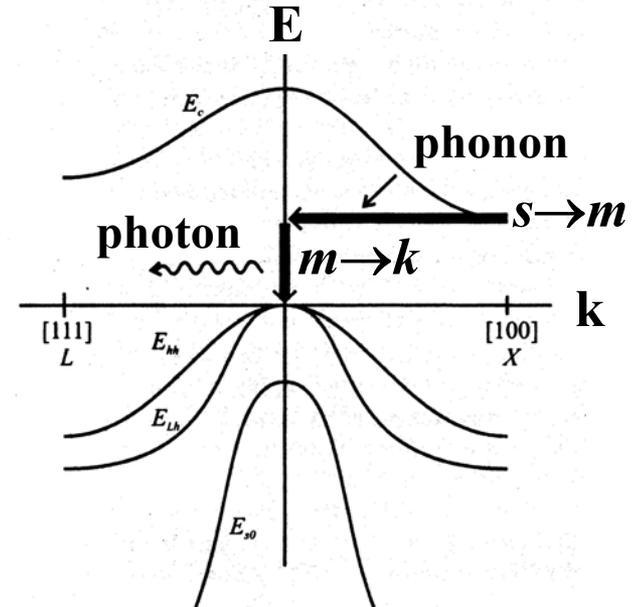
Example of second-order transition

First-order transition



Optical recombination for **direct-gap** semiconductors

Second-order transition



Optical recombination for **indirect-gap** semiconductors

- For indirect semiconductors such as Si and Ge, radiative transitions cannot occur to first order since the matrix element of $\langle k|V|s \rangle$ vanishes because the momentum is not conserved.
- The recombination can occur to second order through phonon-assisted process but the overall probability is low. This is why Si and Ge exhibit weak luminescence efficiency compared to direct-gap semiconductors.