$$\Rightarrow \sum_{k=1}^{\infty} a_k(t) E_k^{(0)} \phi_k + \sum_{k=1}^{\infty} a_k(t) \hat{H}^{(1)}(t) \phi_k = -\frac{\hbar}{i} \sum_{k=1}^{\infty} \left[\dot{a}_k \phi_k + a_k \frac{\partial \left(\psi_k e^{-\frac{iE_k^{(0)} t}{\hbar}} \right)}{\partial t} \right]$$

$$\Rightarrow \sum_{k=1}^{\infty} a_k E_k^{(0)} \phi_k + \sum_{k=1}^{\infty} a_k \hat{H}^{(1)} \phi_k = -\frac{\hbar}{i} \sum_{k=1}^{\infty} \left[\dot{a}_k \psi_k e^{-\frac{iE_k^{(0)} t}{\hbar}} - \frac{i}{\hbar} E_k^{(0)} a_k \phi_k \right]$$

$$\Rightarrow \sum_{k=1}^{\infty} a_k(t) \hat{H}^{(1)}(t) \psi_k e^{-\frac{iE_k^{(0)} t}{\hbar}} = -\frac{\hbar}{i} \sum_{k=1}^{\infty} \dot{a}_k(t) \psi_k e^{-\frac{iE_k^{(0)} t}{\hbar}}$$

Multiply by $\Psi_q^{\star}$ and integrate. Will recognize “q” as an empty state to fill by a transition.

$$\sum_{k=1}^{\infty} a_k(t) \langle \psi_q | \hat{H}^{(1)} | \psi_k \rangle e^{-\frac{iE_k^{(0)} t}{\hbar}} = -\frac{\hbar}{i} \sum_{k=1}^{\infty} \dot{a}_k(t) \underbrace{\langle \psi_q | \psi_k \rangle}_{\delta_{qk}} e^{-\frac{iE_k^{(0)} t}{\hbar}} = -\frac{\hbar}{i} \dot{a}_q(t) e^{-\frac{iE_q^{(0)} t}{\hbar}}$$

Rearrange for $\dot{a}_q(t)$

$$\dot{a}_q(t) = \frac{\partial a_q(t)}{\partial t} = -\frac{i}{\hbar}\sum_{k=1}^{\infty} a_k(t) H_{qk}^{(1)} e^{-\frac{i\left(E_k^{(0)} - E_q^{(0)}\right)t}{\hbar}}$$

= **EXACT** result

= a set of **totally coupled** first order linear differential equations which, in principle, could be solved; for example, by Laplace Transform techniques

However, we can **decouple** the equations by writing each coefficient as a perturbation expansion:

$$a_q(t) = a_q^{(0)}(t) + a_q^{(1)}(t) + a_q^{(2)}(t) + \ldots$$

Now substitute and regroup according to order of the perturbation:

$$\left(\dot{a}_q^{(0)}(t)+\dot{a}_q^{(1)}(t)+\dot{a}_q^{(2)}(t)+\ldots\right)=-\frac{i}{\hbar}\sum_{k=1}^{\infty}\left(a_k^{(0)}(t)+a_k^{(1)}(t)+a_k^{(2)}(t)+\ldots\right)H_{qk}^{(1)}(t)e^{\frac{i\left(E_k^{(0)}-E_q^{(0)}\right)t}{\hbar}}$$

zero[th] order $\qquad \dot{a}_k^{(0)}(t)=0$

first order $\qquad \dot{a}_k^{(1)}(t)=-\frac{i}{\hbar}\sum_{k=1}^{\infty}a_k^{(0)}(t)H_{qk}^{(1)}(t)e^{-\frac{i\left(E_k^{(0)}-E_q^{(0)}\right)t}{\hbar}}$

second order $\qquad \dot{a}_k^{(2)}(t)=-\frac{i}{\hbar}\sum_{k=1}^{\infty}a_k^{(1)}(t)H_{qk}^{(1)}(t)e^{-\frac{i\left(E_k^{(0)}-E_q^{(0)}\right)t}{\hbar}}$

etc.

Successive solution: find zero[th] order solution; substitute into first order equation; find first-order solution; substitute into second order equation, and so on.

Note: $a_q(t=0)=\delta_{qj} \Rightarrow \dot{a}_q(t=0)=0 \quad \therefore a_q^{(n)}(t=0)=const\ \delta_{qj}$

Zero^th order solution

$$\dot{a}_q^{(0)}(t)=0 \Rightarrow a_q^{(0)}(t)-a_q^{(0)}(0)=0$$

$$\Rightarrow a_q^{(0)}(t)=a_q^{(0)}(0)=\delta_{qj}$$

First order solution

$$\dot{a}_q^{(1)}(t)=-\frac{i}{\hbar}\sum_{k=1}^{\infty}a_k^{(0)}(t)H_{qk}^{(1)}(t)e^{-\frac{i\left(E_k^{(0)}-E_q^{(0)}\right)t}{\hbar}}$$

$$=-\frac{i}{\hbar}\sum_{k=1}^{\infty}\delta_{kj}(t)H_{qk}^{(1)}(t)e^{-\frac{i\left(E_k^{(0)}-E_q^{(0)}\right)t}{\hbar}}$$

$$\Rightarrow \dot{a}_q^{(1)} = -\frac{i}{\hbar} H_{qj}^{(1)}(t) e^{-\frac{i\left(E_j^{(0)} - E_q^{(0)}\right)t}{\hbar}} \qquad (q \neq j)$$

$$\Rightarrow a_q^{(1)}(t) - a_q^{(1)}(0) = -\frac{i}{\hbar} \int_0^t H_{qj}^{(1)}(t) e^{-\frac{i\left(E_j^{(0)} - E_q^{(0)}\right)t}{\hbar}} dt$$

Remember $a_q^{(1)}(0)=0$ since $q \neq j$

$$\therefore a_q^{(1)}(t) = -\frac{i}{\hbar} \int_0^t H_{qj}^{(1)}(t) e^{-\frac{i\left(E_j^{(0)} - E_q^{(0)}\right)t}{\hbar}} dt = -\frac{i}{\hbar} \int_0^t H_{qj}^{(1)}(t) e^{-i\omega_{jq}t} dt; \quad \hbar\omega_{jq} = E_j^{(0)} - E_k^{(0)}$$

Could continue, but we won't!!!

Therefore to first order:

$$a_q(t) = a_q^{(0)}(t) + a_q^{(1)}(t) = 0 - \frac{i}{\hbar} \int_0^t H_{qj}^{(1)}(t) e^{-i\omega_{jq}t} dt \qquad q \neq j$$

This allows us to calculate the transition probability, $P_q(t)$, from state j (with $a_j(0)=1$) to any state q (with $a_q(0)=0$) as:

$$P_q(t) = \left|a_q(t)\right|^2 = \left|a_q^{(0)}(t) + a_q^{(1)}(t) + a_q^{(2)}(t) + \ldots\right|^2$$

$$\approx \left|a_q^{(1)}(t)\right|^2 \quad + \text{ terms of order 3 or higher}$$

Have solved the problem in principle and approximately as long as we can:

1. Evaluate $$H_{qj}^{(1)}(t) = \left\langle \psi_q \,|\, \hat{H}^{(1)}(t) \,|\, \psi_j \right\rangle$$

2. Evaluate $$a_q^{(1)}(t) = -\frac{i}{\hbar}\int_0^t H_{qj}^{(1)} e^{i\omega_{qj}t}\,dt$$

Note: transition probability = 0 if $H_{qj}^{(1)} = 0$.
Thus, the perturbation $\mathbf{H}^{(1)}(t)$ must "connect" states.
This yields **SELECTION RULES** to first order.

$H_{qj}^{(1)}(t) = 0$ implies a forbidden transition

$H_{qj}^{(1)}(t) \neq 0$ implies an allowed transition

This result works for direct transitions only: $j \rightarrow n \rightarrow q$ not allowed.