CHAPTER 7: APPROXIMATION METHODS FOR TIME-DEPENDENT PROBLEMS

(From Cohen-Tannoudji, Chapter XIII)
A. STATEMENT OF THE PROBLEM

Consider a system with Hamiltonian $\hat{H}_0$; its eigenvalues and eigenvectors are

$$\hat{H}_0 |\varphi_n\rangle = E_n |\varphi_n\rangle \quad (7.1)$$

($\hat{H}_0$ is discrete and non-degenerate for simplicity.)

At $t = 0$, a perturbation is applied

$$\hat{H}(t) = \hat{H}_0 + W(t) = \hat{H}_0 + \lambda \hat{W}(t) \quad (7.2)$$

where $\lambda \ll 1$, and $\hat{W}(t) = 0$ for $t < 0$:

- $t < 0$: stationary state $|\varphi_i\rangle$ is eigenstate of $\hat{H}_0$
- $t = 0$: $W(t)$
- $t > 0$: evolution starts $|\varphi_i\rangle$ is not eigenstate of $\hat{H}$

final state $|\psi(t)\rangle$
What is the probability \( P_{fi}(t) \) of finding the system in another eigenstate \( |\varphi_f\rangle \) of \( \hat{H}_0 \) at time \( t \)?

Treatment: solve the Schrödinger equation (S. E.)

\[
i\hbar \frac{d}{dt} |\psi(t)\rangle = \left[ \hat{H}_0 + \lambda \hat{W}(t) \right] |\psi(t)\rangle
\]

(7.3)

with the initial condition \( |\psi(0)\rangle = |\varphi_i\rangle \)

\[
\Rightarrow P_{fi}(t) = \left| \langle \varphi_f | \psi(t) \rangle \right|^2
\]

(7.4)

In generally this problem is not rigorously soluble!

\( \Rightarrow \) we need APPROXIMATION METHODS
**B. APPROXIMATE SOLUTION OF THE SCHRÖDINGER EQUATION**

1. **The Schrödinger equation in the \{|\varphi_n\rangle\} representation**

We will use the \{|\varphi_n\rangle\} representation which is convenient as \(|\varphi_i\rangle\) and \(|\varphi_f\rangle\) are eigenstates of \(\hat{H}_0\), and obtain the differential equations for the components of the state vector

\[
|\psi(t)\rangle = \sum_n c_n(t)|\varphi_n\rangle \quad (7.5)
\]

\[
c_n(t) = \langle \varphi_n | \psi(t) \rangle \quad (7.6)
\]

\[
\hat{W}_{nk}(t) = \langle \varphi_n | \hat{W}(t) | \varphi_k \rangle \quad (7.7)
\]

and

\[
\langle \varphi_n | \hat{H}_0 | \varphi_k \rangle = E_n \delta_{nk} \quad (7.8)
\]

We will project both sides of S.E. onto \(|\varphi_n\rangle\) (and use \(\sum_k |\varphi_k\rangle\langle \varphi_k | = \hat{1}\)):

\[
i\hbar \frac{d}{dt} |\psi(t)\rangle = \left[ \hat{H}_0 + \lambda \hat{W}(t) \right] |\psi(t)\rangle \quad (7.9)
\]

\[
\Rightarrow i\hbar \frac{d}{dt} c_n(t) = E_n c_n(t) + \sum_k \lambda \hat{W}_{nk}(t) c_k(t) \quad (7.10)
\]
Changing functions

If $\lambda \hat{W}(t) = 0$ then the equations decouple

$$i\hbar \frac{d}{dt} c_n(t) = E_n c_n(t) \tag{7.11}$$

and yield simple solution

$$c_n(t) = b_n e^{-iE_n t / \hbar} \tag{7.12}$$

where $b_n$ is a constant depending on the initial conditions.

If $\lambda \hat{W}(t) \neq 0$ and $\lambda \ll 1$, we expect the solutions $c_n(t)$ of the full equations to be very close to the solution above (for $\lambda \hat{W}(t) = 0$), and thus if we perform the change of function

$$c_n(t) = b_n(t) e^{-iE_n t / \hbar} \tag{7.13}$$

we can predict that $b_n(t)$ will be slowly varying functions of time.
Substituted into the equation gives

\[
\begin{align*}
    i\hbar e^{-iE_n t/\hbar} \frac{d}{dt} b_n(t) + E_n b_n(t) e^{-iE_n t/\hbar} &= E_n b_n(t) e^{-iE_n t/\hbar} + \sum_k \lambda \hat{W}_{nk}(t) b_k(t) e^{-iE_k t/\hbar} \\
\end{align*}
\]

(7.14)

Multiplying both sides by \( e^{iE_n t/\hbar} \) and introducing the Bohr frequency \( \omega_{nk} = \frac{E_n - E_k}{\hbar} \) gives

\[
\begin{align*}
    i\hbar \frac{d}{dt} b_n(t) &= \lambda \sum_k e^{i\omega_{nk} t} \hat{W}_{nk}(t) b_k(t) \\
\end{align*}
\]

(7.15)
2. Perturbation equations

In general, the solution is not known exactly and, for $\lambda \ll 1$, we try to determine this solution in the form of a power series in $\lambda$

$$b_n(t) = b_n^{(0)}(t) + \lambda b_n^{(1)}(t) + \lambda^2 b_n^{(2)}(t) + \ldots$$ (7.16)

and substitute it into the equation, and set equal the coefficients of $\lambda^r$ on both sides of the equation

i) $r = 0$ :
$$i\hbar \frac{d}{dt} b_n^{(0)}(t) = 0$$ (7.17)

ii) $r \neq 0$ :
$$i\hbar \frac{d}{dt} b_n^{(r)}(t) = \sum_k e^{i\omega_{nk}t/\hbar} \hat{W}_{nk}(t)b_k^{(r-1)}(t)$$ (7.18)

RECURRENCE!
3. Solution to the first order in $\lambda$

a. The state of the system at time $t$

$t < 0$ : $|\varphi_i\rangle$ i.e. $b_i(t) \neq 0, b_k(t) = 0 \forall k \neq i$  

$t = 0$ : \(\hat{H}_0 \rightarrow \hat{H}_0 + \lambda \hat{W}\) and solution of S.E. is continuous at $t = 0$

\[\Rightarrow b_n(t = 0) = \delta_{ni} \quad \forall \lambda\]  

\[\Rightarrow b_n^{(0)}(t = 0) = \delta_{ni}\]  

\[\Rightarrow b_n^{(r)}(t = 0) = 0 \text{ if } r \geq 1\]  

and with $i\hbar \frac{d}{dt} b_n^{(0)}(t) = 0$ we get

0th-order solution: \(b_n^{(0)}(t) = \delta_{ni}\) for all $t > 0$
by integration $b_n^{(1)}(t) = \frac{1}{i\hbar} \int_0^t e^{i\omega_{ni}t'} \hat{W}_{ni}(t') \, dt'$ (7.26)

c_n(t) = b_n(t)e^{-iE_nt/\hbar} \approx (b_n^{(0)}(t) + \lambda b_n^{(1)}(t))e^{-iE_nt/\hbar}$ (7.27)

to the first order time-dependent perturbation theory we get the state of the system at time $t$ calculated to the first order:

$$|\psi(t)\rangle \approx \sum_n c_n(t)|\varphi_n\rangle \quad (7.28)$$
b. The transition probability $P_{if}(t)$

\[
|c_f(t)|^2 = |\langle \varphi_f | \psi(t) \rangle|^2 = P_{if}(t) \tag{7.29}
\]

\[
c_f(t) = b_f(t)e^{-iE_f t/\hbar} \tag{7.30}
\]

\[
\Rightarrow P_{if}(t) = |b_f(t)|^2 \tag{7.31}
\]

where $b_f(t) = b_f^{(0)}(t) + \lambda b_f^{(1)}(t) + \ldots$

Let us assume $|\varphi_i\rangle$ and $|\varphi_f\rangle$ are different (i.e. we are concerned only with transition induced by $\lambda \hat{W}$ between two distinct stationary states of $\hat{H}_0$):

$b_f^{(0)}(t) = 0$ and consequently

\[
P_{if}(t) = \lambda^2 |b_f^{(1)}(t)|^2 \tag{7.32}
\]
and using the formula for $b_n^{(1)}(t)$ we get

$$P_{if}(t) = \frac{1}{\hbar^2} \left| \int_0^t e^{i\omega_{fi}t'} \frac{W_{fi}(t')}{W(t) = \lambda \hat{W}} \, dt' \right|^2$$  \hspace{1cm} (7.33)

Consider the function $\tilde{W}_{fi}(t')$ which is zero for $t' < 0$ and $T' > t$ and is equal to $W_{fi}(t')$ for $0 \leq t' \leq t$.

$\tilde{W}_{fi}(t')$ is the matrix element of the perturbation "seen" by the system between the time $t = 0$ and the measurement time $t$, when we try to determine if the system is in the state $|\varphi_f\rangle$.

$P_{if}(t)$ is proportional to the square of the modulus of the Fourier transform of the perturbation actually "seen" by the system, $\tilde{W}_{fi}(t)$. 
C. SPECIAL CASE: A SINUSOIDAL OR CONSTANT PERTURBATION

\[ \hat{W}(t) = \hat{W} \sin \omega t \] or
\[ \hat{W}(t) = \hat{W} \cos \omega t \]
\( \hat{W} \) is a time independent observable and \( \omega \) a constant angular frequency.

(Example: electromagnetic wave of angular frequency \( \omega \).)

\( \mathcal{P}_{if}(t) \) is the probability, induced by monochromatic radiation, of a transition between the initial state \( |\psi_i\rangle \) and the final state \( |\psi_f\rangle \).

\[ \hat{W}_{fi}(t) = \hat{W}_{fi} \sin \omega t = \frac{\hat{W}_{fi}}{2i} \left( e^{i\omega t} - e^{-i\omega t} \right) \]  

(7.34)

\( \hat{W}_{fi} \) is a time independent complex number and

\[ b_n^{(1)}(t) = -\frac{\hat{W}_{ni}}{2\hbar} \int_0^t \left[ e^{i(\omega_{ni}+\omega)t'} - e^{i(\omega_{ni}-\omega)t'} \right] dt' \]  

(7.35)
\[
\frac{\hat{W}_{ni}}{2i\hbar} \left[ \frac{1 - e^{i(\omega_{ni} + \omega)t}}{\omega_{ni} + \omega} - \frac{1 - e^{i(\omega_{ni} - \omega)t}}{\omega_{ni} - \omega} \right]
\]

(7.36)

The transition probability becomes

\[
P_{if}(t; \omega) = \lambda^2 \left| b_f^{(1)}(t) \right|^2 = \frac{|W_{fi}|^2}{4\hbar^2} \left| \frac{1 - e^{i(\omega_{fi} + \omega)t}}{\omega_{fi} + \omega} - \frac{1 - e^{i(\omega_{fi} - \omega)t}}{\omega_{fi} - \omega} \right|^2
\]

(7.37)

\(P_{if}\) depends on the frequency of the perturbation

If \(\hat{W}_{fi}(t) = \hat{W}_{fi} \cos \omega t\),

\[
P_{if}(t; \omega) = \frac{|W_{fi}|^2}{4\hbar^2} \left| \frac{1 - e^{i(\omega_{fi} + \omega)t}}{\omega_{fi} + \omega} \right|^2 + \left| \frac{1 - e^{i(\omega_{fi} - \omega)t}}{\omega_{fi} - \omega} \right|^2
\]

(7.38)
Constant perturbation $\omega = 0$

\[
\mathcal{P}_{if}(t; \omega) = \frac{|W_{fi}|^2}{\hbar^2 \omega_{fi}^2} \left| 1 - e^{i\omega_{fi}t} \right|^2 = \frac{|W_{fi}|^2}{\hbar^2} F(t; \omega_{fi}) \quad (7.39)
\]

\[
F(t; \omega_{fi}) = \left[ \sin\left(\omega_{fi}t/2\right) / \omega_{fi}/2 \right]^2 \quad (7.40)
\]
2. Sinusoidal perturbation which couples discrete states: resonance
   a. Resonant nature of the transition probability
   When $t$ is fixed, $P_{ij}(t; \omega)$ is a function of one variable $\omega$. This function has a maximum for $\omega \approx \omega_f$ or $\omega \approx -\omega_f$; this is a resonance phenomenon (choose $\omega \geq 0$)
\[ \mathcal{P}_{if}(t; \omega) = \frac{|\hat{W}_{fi}|^2}{4\hbar^2} \left| \frac{1 - e^{i(\omega_{fi} + \omega)t}}{\omega_{fi} + \omega} - \frac{1 - e^{i(\omega_{fi} - \omega)t}}{\omega_{fi} - \omega} \right|^2 \]  

\[ A_+ = -ie^{i(\omega_{fi} + \omega)t/2} \frac{\sin \left[ \left( \omega_{fi} + \omega \right)t/2 \right]}{\left( \omega_{fi} + \omega \right)/2} \]  

goes to zero for \( \omega = -\omega_{fi} \) 

This term is anti-resonant for \( \omega = \omega_{fi} \) (and resonant for \( \omega = -\omega_{fi} \))
Resonant term

\[
A_- = -ie^{i(\omega_{fi}-\omega)t/2} \frac{\sin \left[ \left( \frac{\omega_{fi} - \omega}{2} \right) t \right]}{\left( \frac{\omega_{fi} - \omega}{2} \right)}
\]  

(7.43)

Consider the case \(|\omega - \omega_{fi}| \ll \omega_{fi}\) (this is the resonant approximation):

1\textsuperscript{st} order transition probability:

\[
\mathcal{P}_{if}(t; \omega) = \frac{|W_{fi}|^2}{4\hbar^2} F \left( t; \omega - \omega_{fi} \right)
\]  

(7.44)

\[
F \left( t; \omega - \omega_{fi} \right) = \frac{\sin \left[ \left( \omega_{fi} - \omega \right) t/2 \right]}{\left( \omega_{fi} - \omega \right) / 2}
\]  

sinc function  

(7.45)
The diagram illustrates the frequency spectrum with a peak at $\omega_{fi}$. The width of the peak is given by $\Delta \omega \approx \frac{4\pi}{t}$. The equations $(\omega - \omega_{fi})t/2 = \pi$ and $(\omega - \omega_{fi})t/2 = 3\pi/2$ indicate the positions of relevant points on the spectrum.
b. The resonance width and time-energy uncertainty relation

The most of the resonant peak is concentrated around the resonant frequency $\omega_{fi}$, for example at $\frac{(\omega-\omega_{fi})t}{2} = \frac{3\pi}{2}$ we get the transition probability $\frac{|W_{fi}|^2 t^2}{9\pi^2\hbar^2}$ which is approximately 5% of the transition probability at the resonance.

We can define the width of the resonant peak as the difference between the frequencies of the minima of $P_{if}$ around the resonant frequency, see the figure, then

$$\Delta\omega \approx \frac{4\pi}{t}$$  \hspace{1cm} (7.46)

which is analogous to the time-energy uncertainty relation $\Delta E = \hbar\Delta\omega \approx \frac{\hbar}{t}$.
c. Validity of the perturbation treatment

a) Discussion of the resonant approximation

\( A_+ \) has been neglected relative to \( A_- \): \n\[ |A_-(\omega)|^2 \text{ sinc function} \]

\[
|A_+(\omega)|^2 = |A_-(\omega f_i)|^2 \ll |A_-(-\omega)|^2 \]

(7.47)

The resonant approximation is justified on the condition

\[
2 |\omega_{fi}| \gg \Delta \omega \]

(7.48)

that is

\[
\sqrt{t} \quad \text{duration of the perturbation} \gg \frac{1}{|\omega_{fi}|} \approx \frac{1}{\omega} \quad \text{oscillation period} \]

(7.49)
b) Limits of the first-order calculations

If \( t \) becomes too large, the first-order approximation can cease to be valid (i.e. giving

infinit transition probability which is physically a nonsense):

\[
\lim_{t \to \infty} P_{if}(t; \omega = \omega_{fi}) = \lim_{t \to \infty} \frac{|W_{fi}|^2}{4\hbar^2} t^2 = \infty
\]  

(7.50)

For the first-order approximation to be valid at resonance, \( P_{if}(t; \omega = \omega_{fi}) \ll 1 \):

\[
t \ll \frac{\hbar}{|W_{fi}|}
\]  

(7.51)
3. Coupling with the states of the continuum

$E_f$ belongs to a continuous part of the spectrum of $\hat{H}_0$

\[\downarrow\]

We cannot measure the probability of finding the system in a well-defined state $|\varphi_f\rangle$ at time $t$

\[\downarrow\]

We have to integrate over probability density $|\langle \varphi_f | \psi(t) \rangle|^2$ over a certain group of final states.
a. Integration over a continuum of final states; density of states

a) Example
– spinless particle of mass $m$
– scattering by a potential $W(\vec{r})$

$E = \frac{\vec{p}^2}{2m}, |\psi(t)\rangle$ can be expanded in terms of $|\vec{p}\rangle$
The corresponding wavefunctions are plane waves

$$\langle \vec{r}|\vec{p}\rangle = \left(\frac{1}{2\pi\hbar}\right)^{3/2} e^{i\vec{p}\cdot\vec{r}/\hbar}$$ (7.52)

The probability density

$$|\langle \vec{p}|\psi(t)\rangle|^2$$ (7.53)
Detector gives a signal when the particle is scattered with the momentum $\vec{p}_f$ but since it has a finite aperture it really gives the signal when the particle has momentum in a domain $D_f$ of $\vec{p}$-space around $\vec{p}_f$ ($\delta \Omega_f, \delta E_f$)

$$\delta \mathcal{P}(\vec{p}_f, t) = \int_{\vec{p}_f \in D_f} d^3 \vec{p} |\langle \vec{p} | \psi(t) \rangle|^2$$  \hspace{1cm} (7.54)$$

$$d^3 \vec{p} = p^2 dp \underbrace{d\Omega}_{\text{solid angle around } \vec{p}_f} = \frac{\rho(E)}{dE} dEd\Omega$$ \hspace{1cm} (7.55)

Density of final states

$$\rho(E) = \frac{p^2 dp}{dE} = \frac{p^2 m}{p} = m \sqrt{2mE}$$

$$\delta \mathcal{P}(\vec{p}_f, t) = \int_{\Omega \in \delta \Omega_f, E \in \delta E_f} d\Omega dE \rho(E) |\langle \vec{p} | \psi(t) \rangle|^2$$  \hspace{1cm} (7.56)
b) The general case

Eigenstates of $\hat{H}_0$, labeled by a continuous set of indices

$$\langle \alpha | \alpha' \rangle = \delta(\alpha - \alpha') \quad (7.57)$$

at time $t$: $|\psi(t)\rangle$

$$\delta P(\alpha_f, t) = \int_{\alpha \in D_f} d\alpha |\langle \alpha | \psi(t) \rangle|^2 \quad (7.58)$$

Change variables and introduce density of final states

$$d\alpha = \rho(\beta, E) d\beta dE \quad (7.59)$$

$$\delta P(\alpha_f, t) = \int_{\beta \in \delta\beta_f, E \in \delta E_f} d\beta dE \rho(\beta, E) |\langle \beta, E | \psi(t) \rangle|^2 \quad (7.60)$$
Fermi’s Golden Rule

Let $|\psi(t)\rangle$ be the normalized state vector of the system at time $t$.

Consider a system which is initially in an eigenstate $|\varphi_i\rangle$ of $\hat{H}_0$ (in discrete part of spectrum)

$$\delta P(\varphi_i, \alpha_f, t) = ?$$  \hspace{1cm} (7.61)

The calculations for the case of a sinusoidal or constant perturbation remain valid when the final state of the system belongs to the continuous spectrum of $\hat{H}_0$
For $W$ constant

$$|\langle \beta, E | \psi(t) \rangle|^2 = \frac{1}{\hbar^2} |\langle \beta, E | W | \psi(t) \rangle|^2 F \left( t; \frac{E - E_i}{\hbar} \right)$$  \hspace{1cm} \text{(7.62)}

$E$ – energy of the state $|\beta, E \rangle$

$E_i$ – energy of the state $|\varphi_i \rangle$

$$\delta \mathcal{P} (\varphi_i, \alpha_f, t) = \frac{1}{\hbar^2} \int_{\beta \in \delta \beta_f, E \in \delta E_f} \mathrm{d} \beta \mathrm{d} E \rho (\beta, E) |\langle \beta, E | W | \psi(t) \rangle|^2 F \left( t; \frac{E - E_i}{\hbar} \right)$$  \hspace{1cm} \text{(7.63)}

$F \left( t; \frac{E - E_i}{\hbar} \right)$ varies rapidly about $E = E_i$; for sufficiently large $t$, this function can be approximated, to within a constant factor, by the $\delta$-function $\delta (E - E_i)$:

$$\lim_{t \to \infty} F \left( t; \frac{E - E_i}{\hbar} \right) = \pi t \delta \left( \frac{E - E_i}{2\hbar} \right) = 2\pi \hbar t \delta (E - E_i)$$  \hspace{1cm} \text{(7.64)}
The function $\rho(\beta, E) |\langle \beta, E | W | \psi(t) \rangle|^2$ varies much more slowly with $E$. We will assume that $t$ is sufficiently large for the variation of this function over an energy interval of width $4\pi\hbar/t$ centered at $E = E_i$ to be negligible.

⇒ We can replace $F \left( t; \frac{E - E_i}{\hbar} \right)$ by $2\pi\hbar t \delta(E - E_i)$ which allows us to integrate over $E$ immediately.
If, in addition, $\delta \beta_f$ is very small, integration over $\beta$ is unnecessary and we get
(a) $E_i \in \delta E_f$

$$\delta \mathcal{P}(\varphi_i, \alpha_f, t) = \delta \beta_f \frac{2\pi}{\hbar} t \left| \langle \beta_f, E_f = E_i | W | \varphi_i \rangle \right|^2 \rho(\beta_f, E_f = E_i)$$  \hspace{0.5cm} (7.65)$$

(b) $E_i \notin \delta E_f$

$$\delta \mathcal{P}(\varphi_i, \alpha_f, t) = 0$$  \hspace{0.5cm} (7.66)$$

⇒ A constant perturbation can induce transitions only between states of equal energies, and thus (b) holds.
The probability (a) increases linearly with $t$.

$\Rightarrow$ We can define

- transition probability per unit time $\delta W(\varphi_i, \alpha_f)$
  
  $$\delta W(\varphi_i, \alpha_f) = \frac{d}{dt} \delta P(\varphi_i, \alpha_f, t)$$  
  (7.67)
  
  which is time independent

- transition probability density per unit time and per unit interval of the variable $\beta_f$
  
  $$w(\varphi_i, \alpha_f) = \frac{\delta W(\varphi_i, \alpha_f)}{\delta \beta_f}$$  
  (7.68)
Fermi’s Golden Rule

\[ w(\varphi_i, \alpha_f) = \frac{2\pi}{\hbar} |\langle \beta_f, E_f = E_i | W | \varphi_i \rangle|^2 \rho(\beta_f, E_f = E_i) \quad (7.69) \]

Assume that \( W \) is a sinusoidal perturbation which couples a state \( |\varphi_i\rangle \) to the continuum of states \( |\beta_f, E_f \rangle \) with energies \( E_f \) close to \( E_i + \hbar \omega \). We can carry out the same procedure as above:

\[ w(\varphi_i, \alpha_f) = \frac{\pi}{2\hbar} |\langle \beta_f, E_f = E_i + \hbar \omega | W | \varphi_i \rangle|^2 \rho(\beta_f, E_f = E_i + \hbar \omega) \quad (7.70) \]