Appendix 4

Stationary Perturbation Theory
(定态微扰论)

Objectives

- To learn the basic principles of **perturbation theory**.
- To learn the applications of **non-degenerate** and **degenerate** perturbation theories.

Appendix 4: Stationary Perturbation Theory (定态微扰论)

➢ Perturbation Theory (微扰论)

❖ Perturbation theory is an **approximate approach** used to solve a quantum problem that **cannot be solved exactly (不能严格求解).**

❖ When we consider a quantum system with Hamiltonian $\widehat{\boldsymbol{H}}$ for which the Schrödinger equation has no **exact solutions (严格解)**, if the system can be divided into two subsystems, i.e., $\widehat{\boldsymbol{H}} = \widehat{\boldsymbol{H}}_{\mathbf{0}} + \widehat{\boldsymbol{H}}'$, where the Schrödinger equation of $\widehat{\boldsymbol{H}}_{\mathbf{0}}$ has exact solutions and the strength of **perturbation (微扰)** $\widehat{\boldsymbol{H}}' = \boldsymbol{\lambda W}$ is very small (i.e., $|\boldsymbol{\lambda}| \ll \mathbf{1}$), we can apply the perturbation theory to obtain the **approximate solutions (近似解)**.

Appendix 4: Stationary Perturbation Theory (定态微扰论)

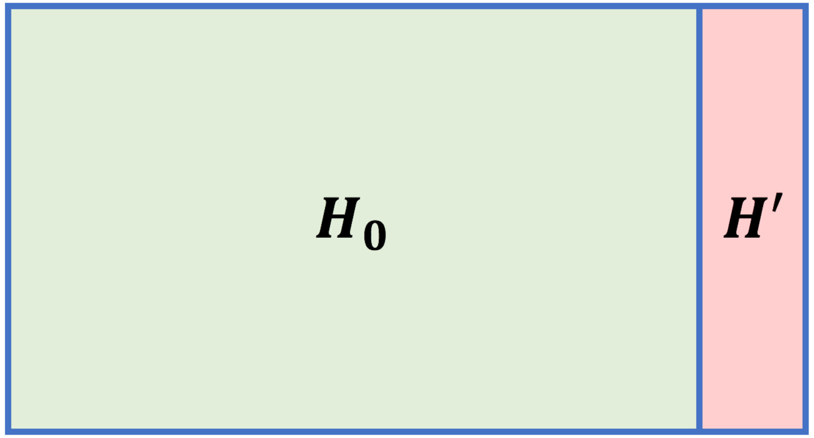
➢ Perturbation Theory (微扰论)

❖ Perturbation theory is an **approximate approach** used to solve a quantum problem that **cannot be solved exactly (不能严格求解).**

$$\hat{H} = \hat{H}_0 + \hat{H}'$$

$$\boxed{\hat{H}_0|\varphi_j\rangle = \varepsilon_j|\varphi_j\rangle}$$ (known已知)

$$\boxed{\hat{H}' = \lambda W \quad (|\lambda| \ll 1)}$$ (perturbation微扰)



$$\boxed{\hat{H}|\psi\rangle = E|\psi\rangle}$$?

Appendix 4: Stationary Perturbation Theory (定态微扰论)

➢ Perturbation Theory (微扰论)

❖ Perturbation theory is an **approximate approach** used to solve a quantum problem that **cannot be solved exactly (不能严格求解).**

$$\left(\hat{H}_0 + \hat{H}'\right)|\psi\rangle = E|\psi\rangle$$

$$\hat{H}' = \lambda W \quad (|\lambda| \ll 1)$$

$\longrightarrow$

$$E(\lambda)$$

$$|\psi(\lambda)\rangle$$

$\longrightarrow$

$$E = E_0 + \lambda E_1 + \lambda^2 E_2 + \cdots$$

$$|\psi\rangle = |\psi_0\rangle + \lambda|\psi_1\rangle + \lambda^2|\psi_2\rangle + \cdots$$

Appendix 4: Stationary Perturbation Theory (定态微扰论)

➢ Perturbation Theory (微扰论)

❖ Perturbation theory is an **approximate approach** used to solve a quantum problem that **cannot be solved exactly (不能严格求解).**

$$\left(\hat{H}_0 + \hat{H}'\right)|\psi\rangle = E|\psi\rangle \longrightarrow$$

$$\lambda^0: \quad \hat{H}_0|\psi_0\rangle = E_0|\psi_0\rangle$$

$$\lambda^1: \quad \left(\hat{H}_0 - E_0\right)|\psi_1\rangle = (E_1 - W)|\psi_0\rangle$$

$$\lambda^2: \quad \left(\hat{H}_0 - E_0\right)|\psi_2\rangle = (E_1 - W)|\psi_1\rangle + E_2|\psi_0\rangle$$

$$\cdots$$

Appendix 4: Stationary Perturbation Theory (定态微扰论)

➢ Perturbation Theory (微扰论)

❖ Perturbation theory is an **approximate approach** used to solve a quantum problem that **cannot be solved exactly (不能严格求解).**

$$E^{(n)} = \lambda^n E_n$$

$$\left|\psi^{(n)}\right\rangle = \lambda^n |\psi_n\rangle$$

$$(n = 0, 1, 2, \cdots)$$

$$\longrightarrow$$

$$E = E^{(0)} + E^{(1)} + E^{(2)} + \cdots$$

$$|\psi\rangle = \left|\psi^{(0)}\right\rangle + \left|\psi^{(1)}\right\rangle + \left|\psi^{(2)}\right\rangle + \cdots$$

$$\left(\hat{H}_0 + \hat{H}'\right)|\psi\rangle = E|\psi\rangle$$

Appendix 4: Stationary Perturbation Theory (定态微扰论)

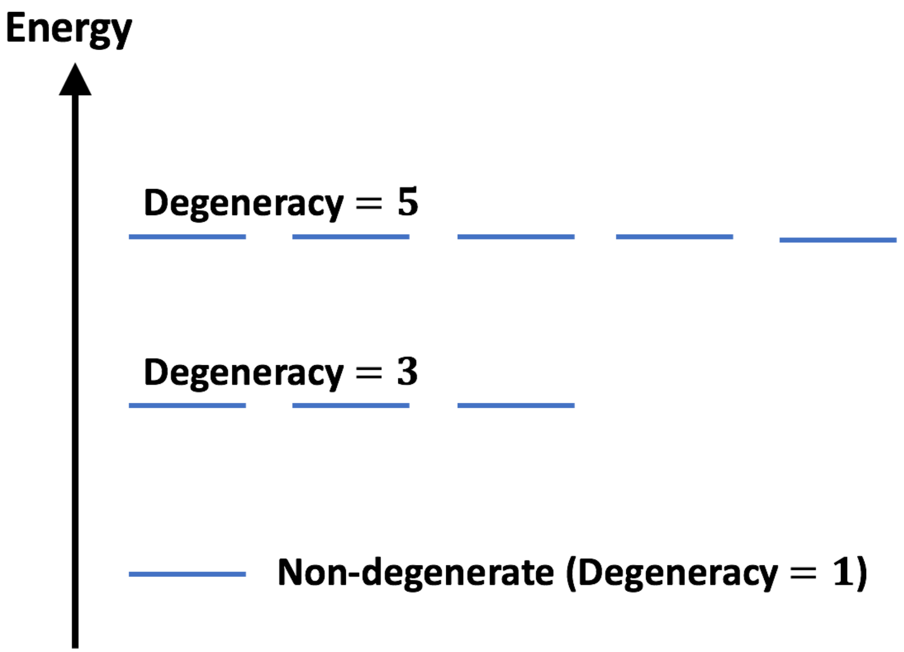
➢ Degeneracy (简并度)

❖ Degenerate (简并):

- One energy level corresponds to **two or more states**.
- The number of the states sharing the same energy level is called **degeneracy (简并度)**.

❖ Non-degenerate (非简并):

- One energy level corresponds to **only one state**.
- The degeneracy is 1.



Non-degenerate Perturbation Theory
(非简并微扰论)

Appendix 4: Stationary Perturbation Theory (定态微扰论)

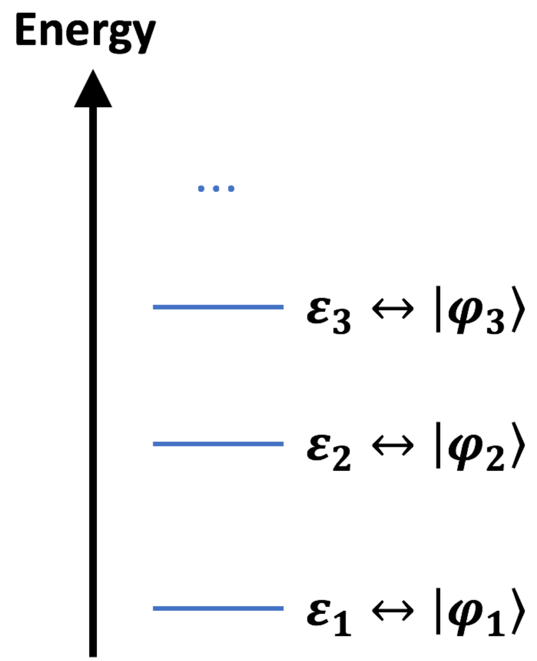
➢ Non-degenerate Perturbation Theory (非简并微扰论)

❖ If all the energy levels of the subsystem $\hat{H}_0$ are **non-degenerate (非简并)**, we can apply the **non-degenerate perturbation theory**.

$$\hat{H}_0|\varphi_j\rangle = \varepsilon_j|\varphi_j\rangle$$

$$\boxed{\varepsilon_j \neq \varepsilon_{j'} \quad (j \neq j')}$$

$$\langle\varphi_{j'}|\varphi_j\rangle = \delta_{j'j}$$



Appendix 4: Stationary Perturbation Theory (定态微扰论)

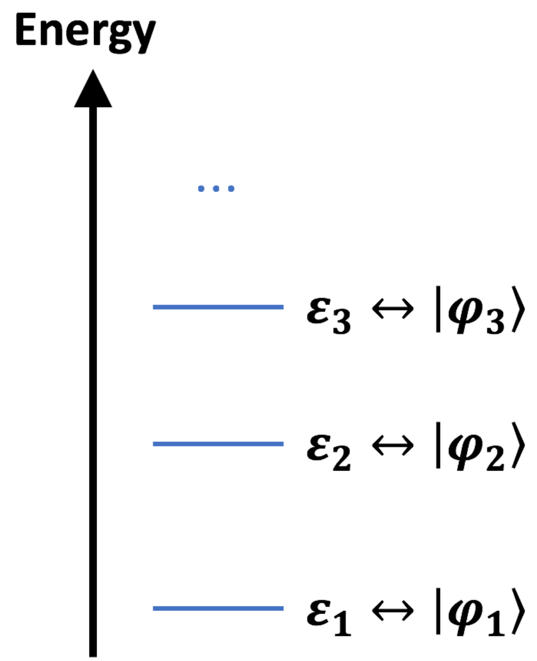
➢ Non-degenerate Perturbation Theory (非简并微扰论)

❖ In the **zeroth-order approximation (零级近似)**:

$$E_k^{(0)} = \varepsilon_k$$

$$\left|\psi_k^{(0)}\right\rangle = |\varphi_k\rangle$$

$$\hat{H}_0 \left|\psi_k^{(0)}\right\rangle = E_k^{(0)} \left|\psi_k^{(0)}\right\rangle$$



Appendix 4: Stationary Perturbation Theory (定态微扰论)

➢ Non-degenerate Perturbation Theory (非简并微扰论)

❖ In the **first-order approximation(一级近似):**

The first-order correction to energy (能量的一级修正):

$$E_k^{(1)} = H'_{kk} = \left\langle \psi_k^{(0)} \middle| \hat{H}' \middle| \psi_k^{(0)} \right\rangle$$

which represents the average of the perturbation on the zeroth-order wavefunctions (微扰在零级波函数下的平均值)!

Appendix 4: Stationary Perturbation Theory (定态微扰论)

- **Non-degenerate Perturbation Theory (非简并微扰论)**

  - In the **first-order approximation(一级近似):**

The first-order correction to wavefunction (波函数的一级修正):

$$\left|\psi_k^{(1)}\right\rangle = \sum_{k' \neq k} \frac{H'_{k'k}}{E_k^{(0)} - E_{k'}^{(0)}} \left|\psi_{k'}^{(0)}\right\rangle$$

The matrix elements: $H'_{k'k} = \left\langle \psi_{k'}^{(0)} \middle| \hat{H}' \middle| \psi_k^{(0)} \right\rangle$

Appendix 4: Stationary Perturbation Theory (定态微扰论)

➢ Non-degenerate Perturbation Theory (非简并微扰论)

❖ In the **second-order approximation(二级近似):**

The second-order correction to energy (能量的二级修正):

$$E_k^{(2)} = \sum_{k' \neq k} \frac{\left|H'_{k'k}\right|^2}{E_k^{(0)} - E_{k'}^{(0)}}$$

The matrix elements: $H'_{k'k} = \left\langle \psi_{k'}^{(0)} \middle| \hat{H}' \middle| \psi_k^{(0)} \right\rangle$

Appendix 4: Stationary Perturbation Theory (定态微扰论)

➢ Non-degenerate Perturbation Theory (非简并微扰论)

❖ In the **second-order approximation(二级近似):**

The second-order correction to wavefunction (波函数的二级修正):

$$\left|\psi_k^{(2)}\right\rangle = \sum_{n\neq k}\left\{\sum_{k'\neq k}\frac{H'_{nk'}H'_{k'k}}{\left[E_k^{(0)}-E_n^{(0)}\right]\left[E_k^{(0)}-E_{k'}^{(0)}\right]} - \frac{H'_{nk}H'_{kk}}{\left[E_k^{(0)}-E_n^{(0)}\right]^2}\right\}\left|\psi_n^{(0)}\right\rangle - \frac{1}{2}\left[\sum_{k'\neq k}\frac{\left|H'_{k'k}\right|^2}{\left[E_k^{(0)}-E_{k'}^{(0)}\right]^2}\right]\left|\psi_k^{(0)}\right\rangle$$

The matrix elements: $H'_{k'k} = \left\langle\psi_{k'}^{(0)}\middle|\hat{H}'\middle|\psi_k^{(0)}\right\rangle$

Appendix 4: Stationary Perturbation Theory (定态微扰论)

➢ Non-degenerate Perturbation Theory (非简并微扰论)

❖ In practice, the **solutions** to the Schrödinger equation by means of the **NDPT** usually read:

$$\boxed{E = E_k^{(0)} + \left\langle \psi_k^{(0)} \middle| \hat{H}' \middle| \psi_k^{(0)} \right\rangle + \sum_{k' \neq k} \frac{\left| H'_{k'k} \right|^2}{E_k^{(0)} - E_{k'}^{(0)}}}$$

(up to the **second-order approximation**)

$$\boxed{|\psi\rangle = \left|\psi_k^{(0)}\right\rangle + \sum_{k' \neq k} \frac{H'_{k'k}}{E_k^{(0)} - E_{k'}^{(0)}} \left|\psi_{k'}^{(0)}\right\rangle}$$

(up to the **first-order approximation**)

Degenerate Perturbation Theory
(简并微扰论)

Appendix 4: Stationary Perturbation Theory (定态微扰论)

➢ Degenerate Perturbation Theory (简并微扰论)

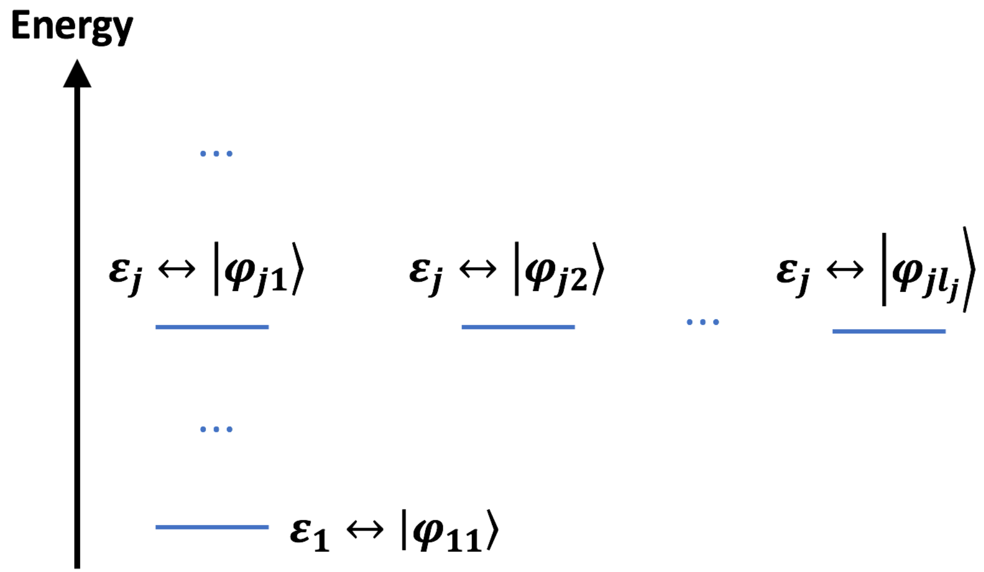
❖ If part of or all the energy levels of the subsystem $\hat{H}_0$ are **degenerate (简并)**, we have to apply the **degenerate perturbation theory**.

$$\hat{H}_0|\varphi_{jl}\rangle = \varepsilon_j|\varphi_{jl}\rangle$$

$$\langle\varphi_{j'l'}|\varphi_{jl}\rangle = \delta_{j'j}\delta_{l'l}$$

$$(l = 1, 2, \cdots, l_j)$$

$$\varepsilon_j \leftrightarrow \begin{cases} |\varphi_{j1}\rangle \\ |\varphi_{j2}\rangle \\ \cdots \\ |\varphi_{jl_j}\rangle \end{cases}$$



Here, l_j denotes the **degeneracy** of the ***j*th** energy levels.

Appendix 4: Stationary Perturbation Theory (定态微扰论)

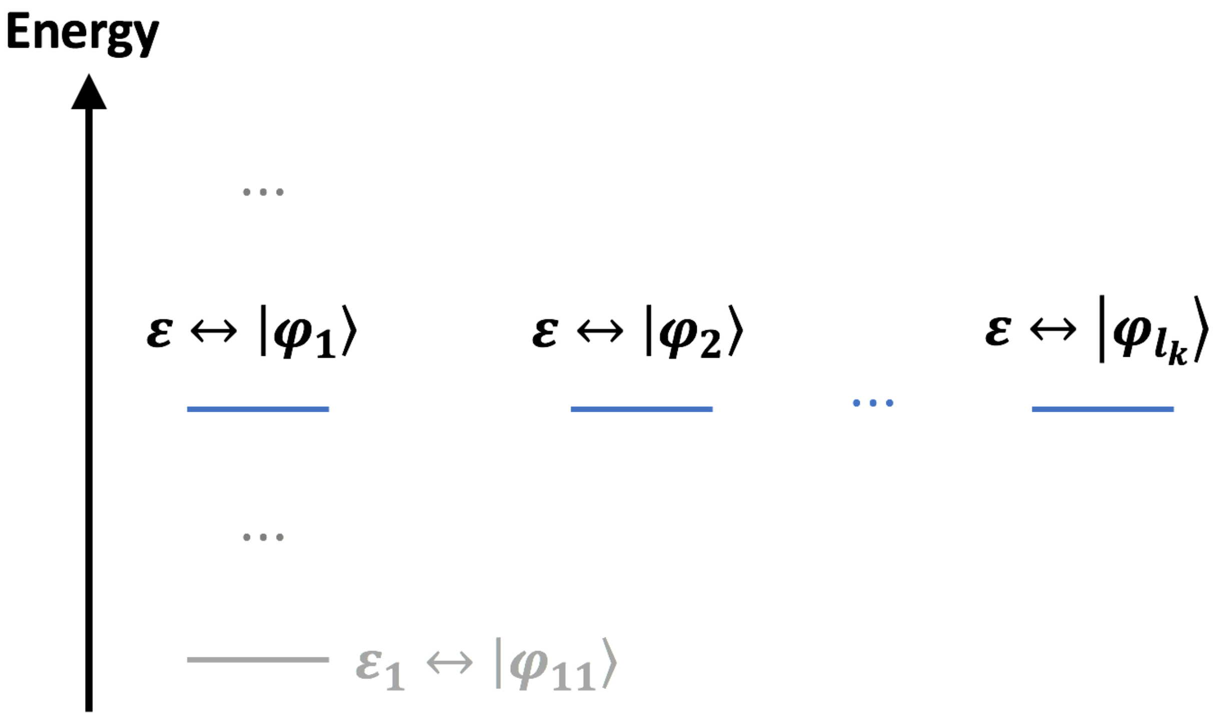
➢ Degenerate Perturbation Theory (简并微扰论)

❖ We consider a given degenerate energy level with degeneracy l_k:

$$\hat{H}_0|\varphi_l\rangle = \varepsilon|\varphi_l\rangle$$

$$\langle\varphi_{l'}|\varphi_l\rangle = \delta_{l'l}$$

$$(l = 1, 2, \cdots, l_k)$$



➢ Degenerate Perturbation Theory (简并微扰论)

❖ In the zeroth-order approximation, we define a new wavefunction by a **linear combination of the degenerate eigen-functions**:

$$|\psi\rangle = \sum_{l=1}^{l_k} \alpha_l |\varphi_l\rangle$$

Here, α_l **(to be determined 待定)** denotes a **coefficient of the linear combination**.

Appendix 4: Stationary Perturbation Theory (定态微扰论)

➢ Degenerate Perturbation Theory (简并微扰论)

❖ By applying to the Schrödinger equation, it is obtained:

$$\left.\begin{aligned} |\psi\rangle &= \sum_{l=1}^{l_k} \alpha_l |\varphi_l\rangle \\ \left(\hat{H}_0 + \hat{H}'\right)|\psi\rangle &= E|\psi\rangle \\ \hat{H}_0|\varphi_l\rangle &= \varepsilon|\varphi_l\rangle \end{aligned}\right\} \xrightarrow{\langle\varphi_{l'}|} \sum_{l=1}^{l_k}\left[(E-\varepsilon)\delta_{l'l} - H'_{l'l}\right]\alpha_l = 0$$

The matrix elements : $H'_{l'l} = \langle\varphi_{l'}|\hat{H}'|\varphi_l\rangle$

Appendix 4: Stationary Perturbation Theory (定态微扰论)

➢ Degenerate Perturbation Theory (简并微扰论)

❖ To obtain **non-trivial solutions (非平庸解)** of α, it is required:

$$\det\left|(E-\varepsilon)\delta_{l'l} - H'_{l'l}\right| = 0 \longrightarrow \boxed{E_n}$$

$$(n = 1, 2, \cdots, l_k)$$

Appendix 4: Stationary Perturbation Theory (定态微扰论)

➢ Degenerate Perturbation Theory (简并微扰论)

❖ By applying back to the Schrödinger equation, it is obtained:

$$\boxed{\boldsymbol{E_n}}$$

$$\left.\begin{aligned} &\sum_{l=1}^{l_k}\left[(E-\varepsilon)\delta_{l'l}-H'_{l'l}\right]\alpha_l = 0 \\ &\sum_{l=1}^{l_k}\alpha_l^2 = 1 \end{aligned}\right\} \longrightarrow \boxed{\alpha_{nl}} \longrightarrow \boxed{|\psi_n\rangle = \sum_{l=1}^{l_k}\alpha_{nl}|\varphi_l\rangle}$$

$$(n = 1, 2, \cdots, l_k)$$

Appendix 4: Stationary Perturbation Theory (定态微扰论)

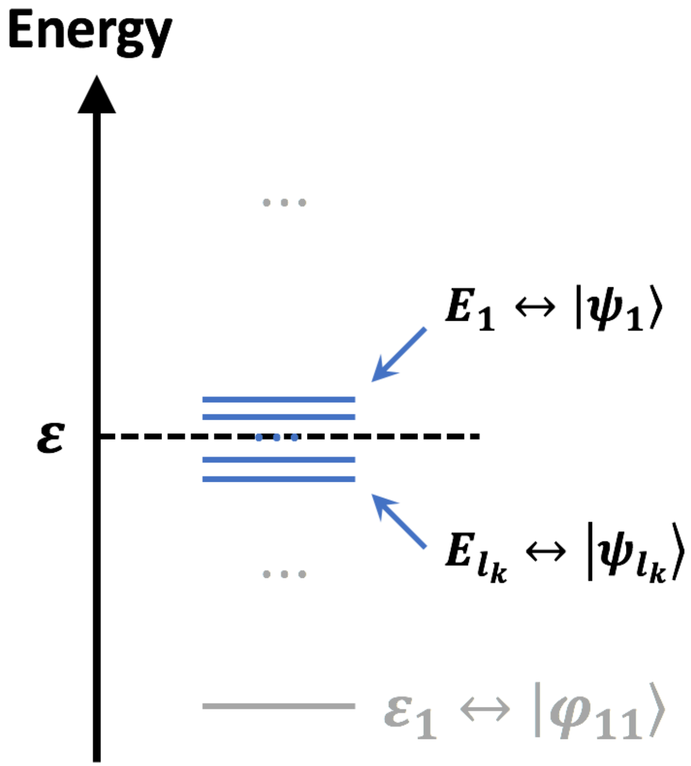
➢ Degenerate Perturbation Theory (简并微扰论)

❖ In practice, the **solutions** to the Schrödinger equation by means of the **DPT** usually read:

$$\boxed{E_n = \varepsilon + \langle \psi_n | \hat{H}' | \psi_n \rangle = \varepsilon + \sum_{l'l} \alpha^*_{nl'} \alpha_{nl} H'_{l'l}}$$

$$\boxed{|\psi_n\rangle = \sum_{l=1}^{l_k} \alpha_{nl} |\varphi_l\rangle} \qquad (n = 1, 2, \cdots, l_k)$$

The matrix elements : $H'_{l'l} = \langle \varphi_{l'} | \hat{H}' | \varphi_l \rangle$



➢ Degenerate Perturbation Theory (简并微扰论)

❖ Mathematically, the degenerate perturbation theory is essentially a **unitary transformation (幺正变换)** by which the perturbation $\boldsymbol{\hat{H}'}$ is **diagonalized (对角化).**

$$\left.\begin{array}{r} \hat{H}_0|\varphi_l\rangle = \varepsilon|\varphi_l\rangle \\ \langle\varphi_{l'}|\varphi_l\rangle = \delta_{l'l} \\ \left(\boldsymbol{\hat{H}_0} + \boldsymbol{\hat{H}'}\right)|\boldsymbol{\varphi_l}\rangle \neq \boldsymbol{E}|\boldsymbol{\varphi_l}\rangle \end{array}\right\} \xrightarrow[\text{Unitary Transformation}]{|\boldsymbol{\psi_n}\rangle = \sum_{l=1}^{l_k} \boldsymbol{\alpha_{nl}}|\boldsymbol{\varphi_l}\rangle} \left\{\begin{array}{l} \left(\boldsymbol{\hat{H}_0} + \boldsymbol{\hat{H}'}\right)|\boldsymbol{\psi_n}\rangle = \boldsymbol{E_n}|\boldsymbol{\psi_n}\rangle \\ \boldsymbol{E_n} = \boldsymbol{\varepsilon} + \langle\boldsymbol{\psi_n}|\boldsymbol{\hat{H}'}|\boldsymbol{\psi_n}\rangle \\ \langle\boldsymbol{\psi_{n'}}|\boldsymbol{\psi_n}\rangle = \boldsymbol{\delta_{n'n}} \end{array}\right.$$

An Example of DPT
(简并微扰论实例)

Appendix 4: Stationary Perturbation Theory (定态微扰论)

➢ Degenerate Perturbation Theory (简并微扰论)

❖ **Example**: 1D nearly-free-electron model at the boundary of the 1st Brillouin zone.

$$\hat{H} = \hat{H}_0 + \hat{H}'$$

$$\hat{H}_0 = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} + \bar{V} = -\frac{\hbar^2}{2m}\frac{d^2}{dx^2} \qquad (\bar{V} = 0)$$

$$\hat{H}' = V(x) - \bar{V} = \Delta V(x)$$

Appendix 4: Stationary Perturbation Theory (定态微扰论)

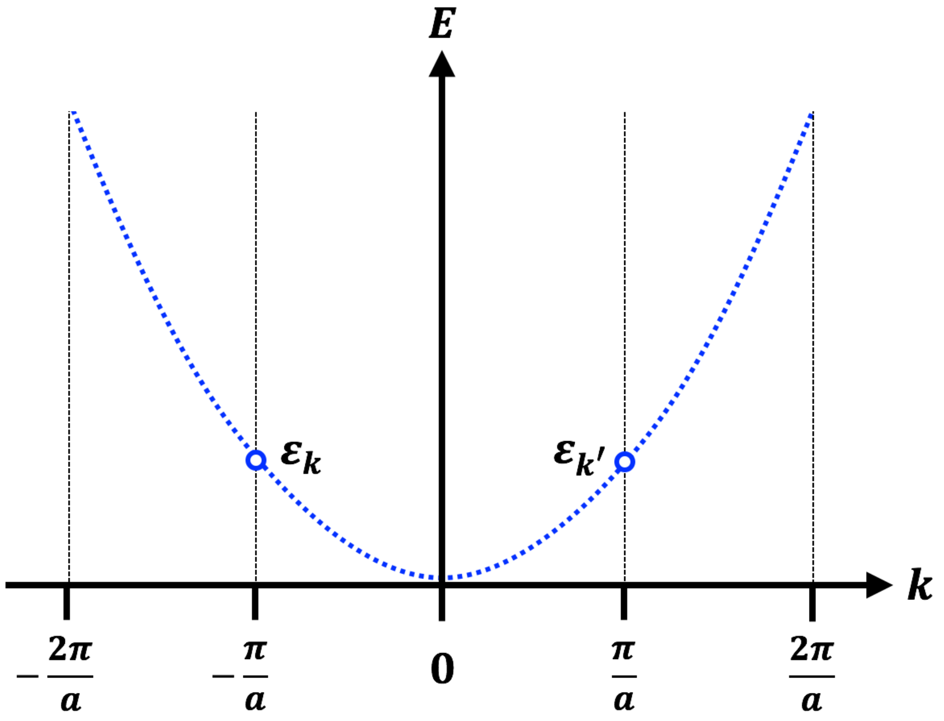
➢ Degenerate Perturbation Theory (简并微扰论)

❖ **Example**: 1D nearly-free-electron model at the boundary of the 1st Brillouin zone.

$$\varepsilon_k = \varepsilon_{k'} = \frac{\hbar^2(\pi/a)^2}{2m}$$

$$|\varphi_k\rangle = \frac{1}{\sqrt{Na}} e^{i\frac{\pi}{a}x} \qquad |\varphi_{k'}\rangle = \frac{1}{\sqrt{Na}} e^{-i\frac{\pi}{a}x}$$

$$\hat{H}_0|\varphi_k\rangle = \varepsilon_k|\varphi_k\rangle \qquad \hat{H}_0|\varphi_{k'}\rangle = \varepsilon_{k'}|\varphi_{k'}\rangle$$



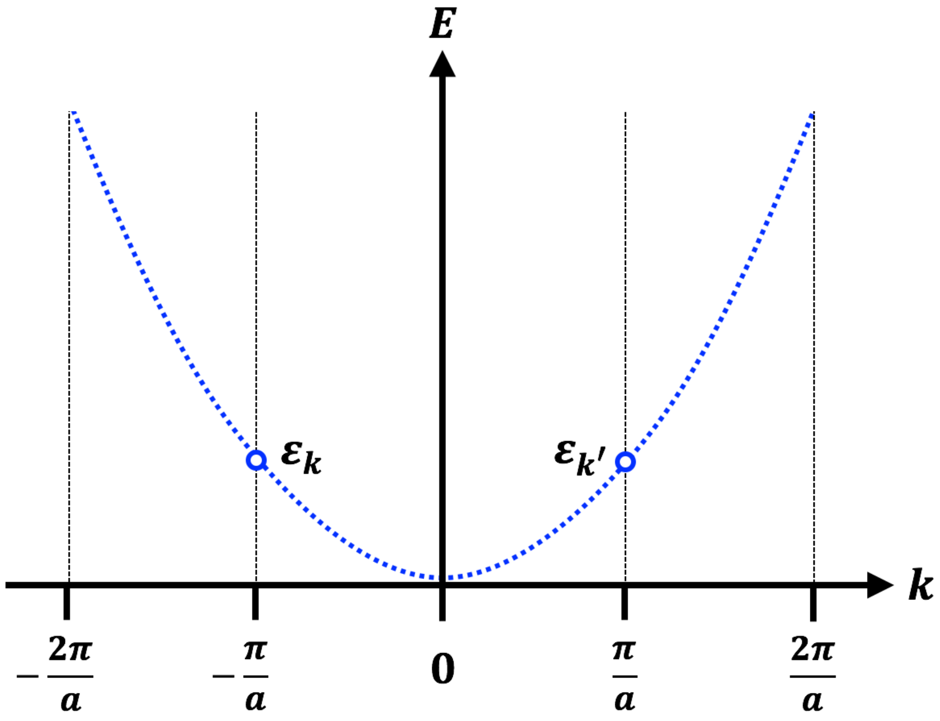
Appendix 4: Stationary Perturbation Theory (定态微扰论)

➢ Degenerate Perturbation Theory (简并微扰论)

❖ **Example**: 1D nearly-free-electron model at the boundary of the 1st Brillouin zone.

The new wavefunctions:

$$|\psi\rangle = \alpha|\varphi_k\rangle + \beta|\varphi_{k'}\rangle$$



Appendix 4: Stationary Perturbation Theory (定态微扰论)

➢ **Degenerate Perturbation Theory (简并微扰论)**

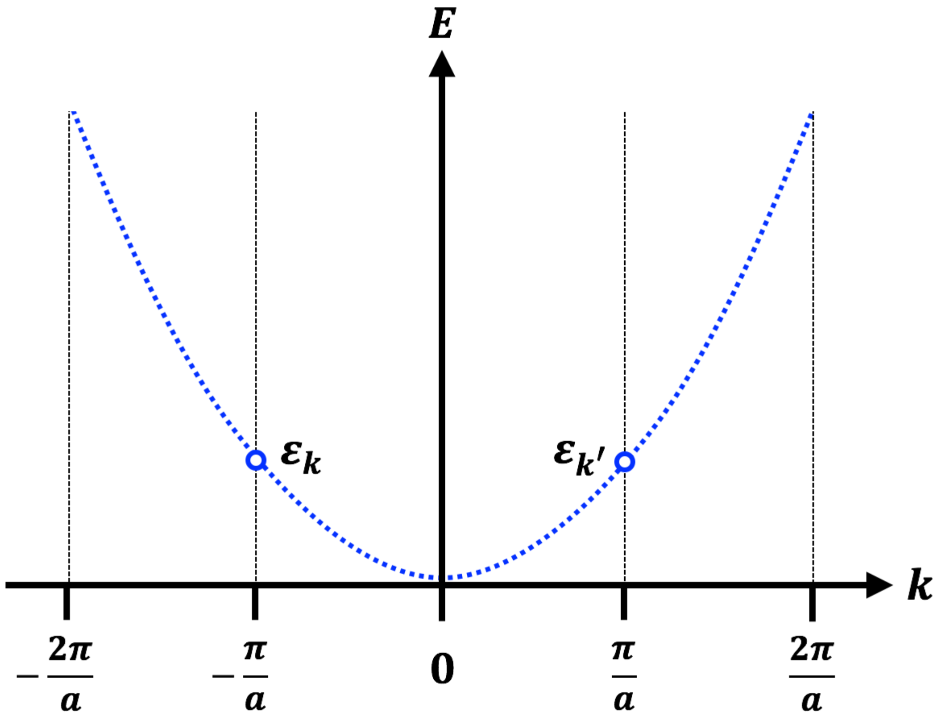
❖ **Example**: 1D nearly-free-electron model at the boundary of the 1st Brillouin zone.

By applying to $(\hat{H}_0 + \hat{H}')|\psi\rangle = E|\psi\rangle$, we obtain:

$$\begin{cases} (\boldsymbol{\varepsilon_k - E})\boldsymbol{\alpha} + \boldsymbol{V_1^*\beta = 0} \\ \boldsymbol{V_1\alpha} + (\boldsymbol{\varepsilon_{k'} - E})\boldsymbol{\beta = 0} \end{cases}$$

$$\rightarrow \quad \begin{vmatrix} \boldsymbol{\varepsilon_k - E} & \boldsymbol{V_1^*} \\ \boldsymbol{V_1} & \boldsymbol{\varepsilon_{k'} - E} \end{vmatrix} = \boldsymbol{0}$$

$$V_1 = \langle \varphi_{k'} | \hat{H}' | \varphi_k \rangle \qquad V_1^* = \langle \varphi_k | \hat{H}' | \varphi_{k'} \rangle$$



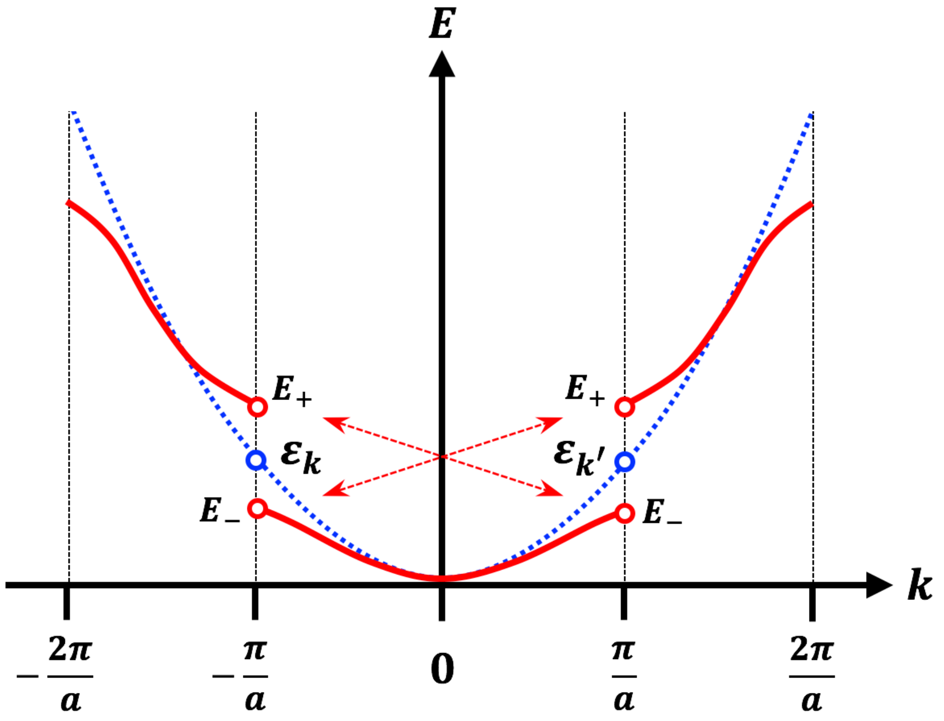
Appendix 4: Stationary Perturbation Theory (定态微扰论)

➢ Degenerate Perturbation Theory (简并微扰论)

❖ **Example**: 1D nearly-free-electron model at the boundary of the 1st Brillouin zone.

By applying to $(\hat{H}_0 + \hat{H}')|\psi\rangle = E|\psi\rangle$, we obtain:

$$\begin{cases} E_+ = \dfrac{1}{2}\left[(\boldsymbol{\varepsilon_k} + \boldsymbol{\varepsilon_{k'}}) + \sqrt{(\boldsymbol{\varepsilon_k} - \boldsymbol{\varepsilon_{k'}})^2 + 4|V_1|^2}\right] = \boldsymbol{\varepsilon_k} + |V_1| \\ E_- = \dfrac{1}{2}\left[(\boldsymbol{\varepsilon_k} + \boldsymbol{\varepsilon_{k'}}) - \sqrt{(\boldsymbol{\varepsilon_k} - \boldsymbol{\varepsilon_{k'}})^2 + 4|V_1|^2}\right] = \boldsymbol{\varepsilon_k} - |V_1| \end{cases}$$



Appendix 4: Stationary Perturbation Theory (定态微扰论)

➢ Degenerate Perturbation Theory (简并微扰论)

❖ **Example**: 1D nearly-free-electron model at the boundary of the 1st Brillouin zone.

By applying to $\left(\hat{H}_0 + \hat{H}'\right)|\psi\rangle = E|\psi\rangle$, we obtain:

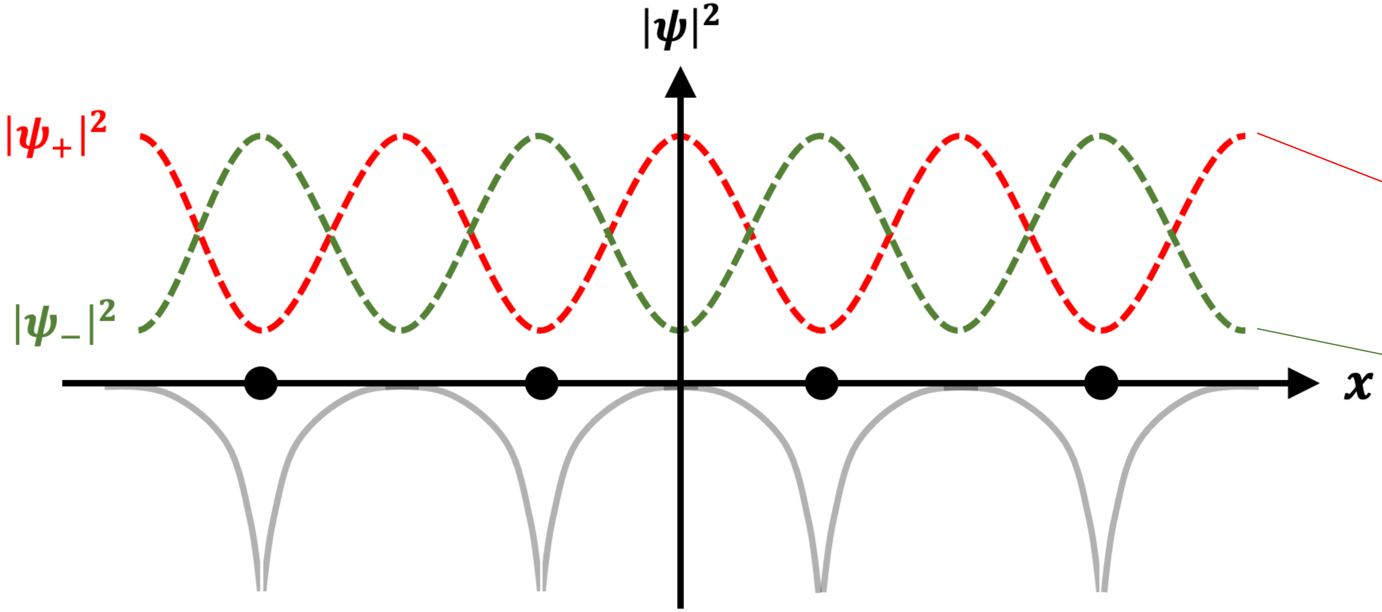
$$\begin{cases} \boldsymbol{\alpha^2 - \beta^2 = 0} \\ \boldsymbol{\alpha^2 + \beta^2 = 1} \end{cases} \rightarrow \begin{cases} \boldsymbol{\alpha = \beta = \dfrac{1}{\sqrt{2}}} \\ \boldsymbol{\alpha = -\beta = \dfrac{1}{\sqrt{2}}} \end{cases} \rightarrow \begin{cases} \boldsymbol{|\psi_+\rangle = \dfrac{1}{\sqrt{2}}(|\varphi_k\rangle + |\varphi_{k'}\rangle)} \\ \boldsymbol{|\psi_-\rangle = \dfrac{1}{\sqrt{2}}(|\varphi_k\rangle - |\varphi_{k'}\rangle)} \end{cases}$$

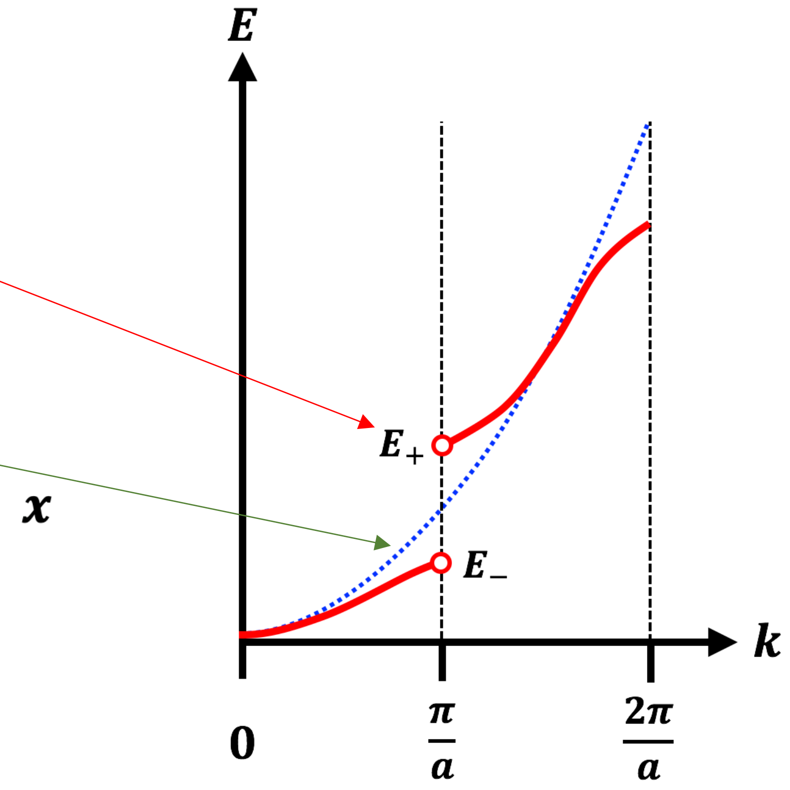
Appendix 4: Stationary Perturbation Theory (定态微扰论)

➢ Degenerate Perturbation Theory (简并微扰论)

❖ **Example**: 1D nearly-free-electron model at the boundary of the 1st Brillouin zone.

The new wavefunctions:





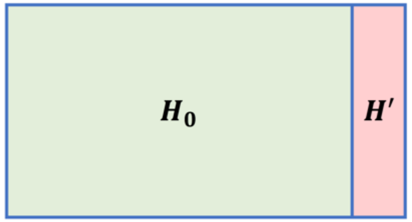
Summary (总结)

Appendix 4: Stationary Perturbation Theory (定态微扰论)

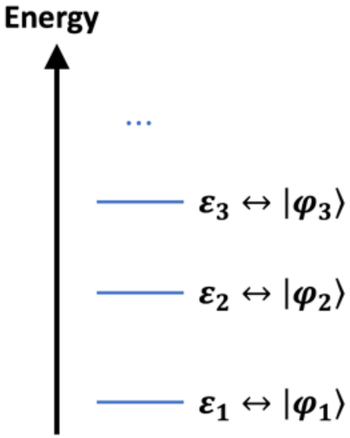
➢ Summary

❖ The basic principles of **perturbation theory**:

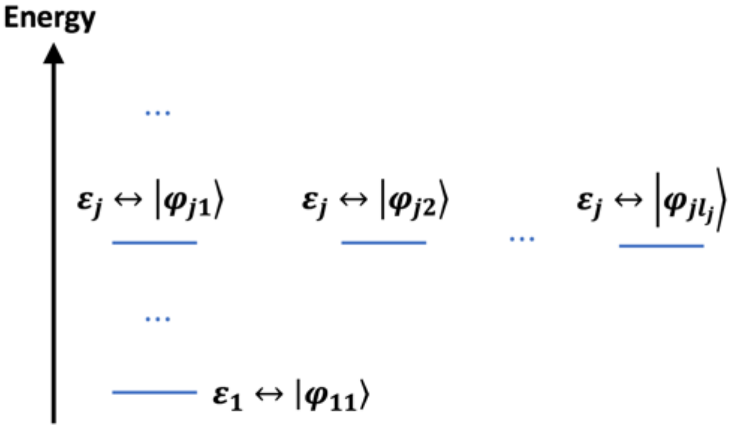
$$\hat{H} = \hat{H}_0 + \hat{H}'$$



❖ **Non-degenerate** and **degenerate** perturbation theories.



Non-degenerate



Degenerate