POSTECH 이성익 교수의
양자 세계에 관한 강연
- 11장 -

편집 도우미: **POSTECH** 학부생 임향택

Chapter 11

Time-Independent Perturbation Theory

Not exactly soluble equation

$$H = H_0 + \lambda H_1$$
$$H_0 \phi_n = E_n^0 \phi_n$$

$$\left(H_0 + \lambda H_1\right)\psi_n = E_n \psi_n$$

ψ_n을 λ의 power 승으로 표시. 단 Convergence는 취급 안함

$\lambda \to 0 \quad \psi_n = \phi_n, \quad E_n = E_{n0}$

Let

$$\psi_n = N(\lambda)\cdot\left\{\phi_n + \sum_{k\neq n} C_{nk}(\lambda)\phi_k\right\}$$

phase $N(\lambda)$ $\qquad N(0)=1, \quad C_{nk}(0)=0$

$$\therefore \begin{array}{l} C_{nk}(\lambda) = \lambda C_{nk}^{(1)} + \lambda^2 C_{nk}^{(2)} + \cdots \\ \quad E_n = E_n^0 + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \cdots \end{array}$$

$$\therefore \begin{array}{l} \left(H_0 + \lambda H_1\right)\left\{\phi_n + \sum_{k\neq n}\lambda C_{nk}^{(1)}\phi_k + \sum_{k\neq n}\lambda^2 C_{nk}^{(2)}\phi_k + \cdots\right\} \\ = \left(E_n^0 + \lambda E_n^1 + \lambda^2 E_n^2 + \cdots\right)\cdot\left\{\phi_n + \sum_{k\neq n}\lambda C_{nk}^{(1)}\phi_k + \sum_{k\neq n}\lambda^2 C_{nk}^{(2)}\phi_k + \cdots\right\} \end{array}$$

$$\lambda: \; H_0 \sum_{k\neq n} C_{nk}^{(1)}\phi_k + H_1\phi_n = E_n^0 \sum_{k\neq n} C_{nk}^{(1)}\phi_k + E_n^{(1)}\phi_n$$

using $H_0 \phi_k = E_k^0 \phi_k$

$$\therefore \sum_{k\neq n} C_{nk}^{(1)} E_k^0 \phi_k + H_1\phi_n = E_n^0 \sum_{k\neq n} C_{nk}^{(1)}\phi_k + E_n^{(1)}\phi_n$$

$$\therefore E_n^{(1)}\phi_n = H_1\phi_n + \sum_{k\neq n}\left(E_k^0 - E_n^0\right)C_{nk}^{(1)}\phi_k$$

Scalar product with ϕ_n

$$\therefore E_n^{(1)} = \langle \phi_n | H | \phi_n \rangle$$

Scalar product with ϕ_m, $m \neq n$

$$\left\langle \phi_m \middle| H_0 \sum_{k\neq n} C_{nk}^{(1)} \phi_k \right\rangle + \langle \phi_m | H_1 | \phi_n \rangle = E_n^0 \sum_{k\neq n} \langle \phi_m | C_{nk}^{(1)} | \phi_k \rangle$$

$$\therefore \left\langle \phi_m \middle| \sum_{k\neq n} E_k^0 C_{nk}^{(1)} \phi_k \right\rangle + \langle \phi_m | H_1 | \phi_n \rangle = E_n^0 C_{nm}^{(1)}$$

$$E_m^0 C_{nm}^{(1)} + \langle \phi_m | H_1 | \phi_n \rangle = E_n^0 C_{nm}^{(1)}$$

$$\therefore C_{nm}^{(1)} = \frac{\langle \phi_m | H_1 | \phi_n \rangle}{E_n^0 - E_m^0}$$

λ^2에 의한 항

$$H_0 \sum_{k\neq n} C_{nk}^{(2)} \phi_k + H_1 \sum_{k\neq n} C_{nk}^{(1)} \phi_k = E_n^0 \sum_{k\neq n} C_{nk}^{(2)} \phi_k + E_n^{(1)} \sum_{k\neq n} C_{nk}^{(1)} \phi_k + E_n^{(2)} \phi_n$$

Scalar product with ϕ_n

$$\therefore \langle \phi_n | H_1 \sum_{k\neq n} C_{nk}^{(1)} | \phi_k \rangle = E_n^{(2)}$$

$$E_n^{(2)} = \sum_{k\neq n} \langle \phi_n | H_1 | \phi_k \rangle C_{nk}^{(1)}$$

$$= \sum_{k\neq n} \langle \phi_n | H_1 | \phi_k \rangle \cdot \frac{\langle \phi_k | H_1 | \phi_n \rangle}{E_n^0 - E_k^0}$$

$$= \sum_{k\neq n} \frac{\left| \langle \phi_n | H_1 | \phi_k \rangle \right|^2}{E_n^0 - E_k^0}$$

a) if ϕ_n is ground state

$$\phi_n^{(2)} = \sum_{k\neq n} \frac{\left| \langle \phi_n | H_1 | \phi_k \rangle \right|^2}{E_n^0 - E_k^0} < 0$$

b) E_n^0와 가까운 쪽에서 더 큰 기여

c) 만약 에너지 높으면 낮아지게
낮으면 높아지게
A tendency of levels to repel each other.

$$1=\langle\psi_n|\psi_n\rangle=N^2(\lambda)\left\{1+\lambda^2\cdot\sum_{k\neq n}\left|C_{nk}^{(1)}\right|^2+\cdots\right\}$$

$N(\lambda)$는 1차 항까지는 zero

$$=\left(1+\lambda^2\square\right)(\qquad\qquad)$$

$$\therefore\psi_n=\phi_n+\sum_{k\neq n}\frac{\langle\phi_k|\lambda H_1|\phi_n\rangle}{E_n^0-E_k^0}\phi_k$$

만약, degenerate case

Orthogonal하게 만들자.

$$\left\langle\phi_m^{(j)}\middle|\phi_n^{(i)}\right\rangle=\delta_{mn}\delta_{ij}$$

$$\psi_n=N(\lambda)\cdot\left\{\sum_i\alpha_i\phi_n^{(i)}+\lambda\sum_{k\neq n}C_{nk}^{(1)}\sum_i\beta_i\phi_k^{(i)}+\cdots\right\}$$

α_i,β_i는 결정되어야 할 양. $H\psi_n=E_n\psi_n$

$$H_0\sum_{k\neq n}C_{nk}^{(1)}\sum_i\beta_i\phi_k^{(i)}+H_1\sum_i\alpha_i\phi_n^{(i)}=E_n^{(1)}\sum_i\alpha_i\phi_n^{(i)}+E_n^0\sum_{k\neq n}C_{nk}^{(1)}\sum_i\beta_i\phi_k^{(i)}$$

$\phi_n^{(j)}$를 product하자.

$$\sum_i\alpha_i\left\langle\phi_n^{(j)}\middle|\lambda H_1\middle|\phi_n^{(i)}\right\rangle=\lambda E_n^{(1)}\alpha_j$$

finite dimensional Eigenvalue problem

$$\sum_i\left\langle\phi_n^{(j)}\middle|H_1\middle|\phi_n^{(i)}\right\rangle\alpha_i=E_n^{(1)}\alpha_j$$

예. two fold degeneracy

$$\left\langle\phi_n^{(j)}\middle|H_1\middle|\phi_n^{(i)}\right\rangle=h_{ji}$$

$$h_{11}\alpha_1+h_{12}\alpha_2=E_n^{(1)}\alpha_1$$
$$h_{21}\alpha_1+h_{22}\alpha_2=E_n^{(1)}\alpha_2$$

$$|\alpha_1|^2+|\alpha_2|^2=1$$

예. 수소원자에서 P상태(same E) $L=1, L_z=1,0,-1$모든 m-value에 대해

만약 외부에서 Electric field를 걸어주면

에너지를 splitting 시킨다. – Stark effect

$$H_0=\frac{p^2}{2\mu}-\frac{ze^2}{r},\ \ \vec{F}=-\nabla H_1 \text{ and } \vec{F}=-eE\hat{z}$$

$$H_1=e\varepsilon z$$

S state$(1,0,0)$

$$\begin{aligned}E_{100}^{(1)}&=e\varepsilon\langle\phi_{100}|z|\phi_{100}\rangle\\&=e\varepsilon\int d^3r\left|\phi_{100}(\vec{r})\right|^2\cdot z\\&=0\end{aligned}$$

Ground state가 degenerate 없으면

$E^{(1)}=0$ $\quad\therefore$ no permanent dipole moment

P state: $n=2$state

$$\phi_{200}=(2a_0)^{-\frac{3}{2}}\left(1-\frac{r}{2a_0}\right)e^{-\frac{r}{2a_0}}Y_{00}$$

$$\phi_{211}=(2a_0)^{-\frac{3}{2}}\cdot 3^{-\frac{1}{2}}\left(\frac{r}{a_0}\right)e^{-\frac{r}{2a_0}}Y_{11}$$

$$\phi_{210}=(2a_0)^{-\frac{3}{2}}\cdot 3^{-\frac{1}{2}}\left(\frac{r}{a_0}\right)e^{-\frac{r}{2a_0}}Y_{10}$$

$$\phi_{21-1}=(2a_0)^{-\frac{3}{2}}\cdot 3^{-\frac{1}{2}}\left(\frac{r}{a_0}\right)e^{-\frac{r}{2a_0}}Y_{1-1}$$

Let

$$\phi_{200}=|1\rangle$$
$$\phi_{211}=|2\rangle$$
$$\phi_{210}=|3\rangle$$
$$\phi_{21-1}=|4\rangle$$

$$\sum_i\alpha_i\left\langle\phi_n^{(j)}\middle|H_1\middle|\phi_n^{(i)}\right\rangle=E_n^{(1)}\alpha_j=\sum_i\alpha_i E_n^{(1)}\delta_{ji}$$

$$\det\left(\langle i|H|j\rangle-E^{(2)}\right)=0$$

$$0=\det\begin{pmatrix} \langle 1|H_1|1\rangle - E_n^{(2)} & \langle 1|H_1|2\rangle & \langle 1|H_1|3\rangle & \langle 1|H_1|4\rangle \\ \langle 2|H_1|1\rangle & \langle 2|H_1|2\rangle - E_n^{(2)} & \langle 2|H_1|3\rangle & \langle 2|H_1|4\rangle \\ \langle 3|H_1|1\rangle & \langle 3|H_1|2\rangle & \langle 3|H_1|3\rangle - E_n^{(2)} & \langle 3|H_1|4\rangle \\ \langle 4|H_1|1\rangle & \langle 4|H_1|2\rangle & \langle 4|H_1|3\rangle & \langle 4|H_1|4\rangle - E_n^{(2)} \end{pmatrix}$$

$\therefore$

$$=\det\begin{pmatrix} -E_n^{(2)} & 0 & \langle 1|H_1|3\rangle & 0 \\ 0 & -E_n^{(2)} & 0 & 0 \\ \langle 3|H_1|1\rangle & 0 & -E_n^{(2)} & 0 \\ 0 & 0 & 0 & -E_n^{(2)} \end{pmatrix}$$

$$\therefore E_n^{(2)}=0 \quad \text{or} \quad \left(E_n^{2(2)}-\left|\langle 1|H_1|3\rangle\right|^2\right)=0$$

$$\therefore E_n^{(2)}=\pm\left|\langle 1|H_1|3\rangle\right|$$

$\therefore \phi_{211,}\phi_{21-1}$ 은 Energy shift 없다.

$$\therefore 0=\begin{pmatrix} -E_n^{(2)} & \langle 1|H_1|3\rangle \\ \langle 3|H_1|1\rangle & -E_n^{(2)} \end{pmatrix}\begin{pmatrix}\alpha_1\\ \alpha_2\end{pmatrix}$$

$$\langle 1|H_1|3\rangle=\int(2a_0)^{-\frac{3}{2}}\cdot 2\cdot\left(1-\frac{r}{2a_0}\right)e^{-\frac{r}{2a_0}}Y_{00}^*\cdot eEz\cdot(2a_0)^{-\frac{3}{2}}\cdot 3^{-\frac{1}{2}}\cdot\left(\frac{r}{a_0}\right)e^{-\frac{r}{2a_0}}Y_{10}r^2dr\sin\theta d\theta d\phi$$

$$=eE(2a_0)^{-3}\cdot 2\cdot 3^{-\frac{1}{2}}\cdot\int\left(1-\frac{r}{2a_0}\right)\left(\frac{r}{a_0}\right)\cdot e^{-\frac{r}{a_0}}r^3dr\int Y_{00}^*\cdot Y_{10}\cdot\cos\theta\cdot\sin\theta d\theta d\phi$$

$$=eE\cdot(-3a_0)$$

$$Y_{10}=\sqrt{\frac{3}{4\pi}}\cos\theta, Y_{00}=\frac{1}{\sqrt{4\pi}}$$

$$\therefore 0=\begin{pmatrix} -E_n^{(2)} & -3a_0eE \\ -3a_0eE & -E_n^{(2)} \end{pmatrix}\begin{pmatrix}\alpha\\ \beta\end{pmatrix}$$

Let $E_n^{(2)}=-3a_0eE$ then $\alpha=\beta$

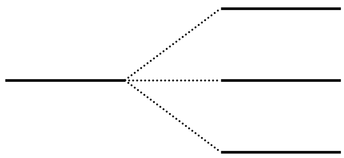
$$\therefore|\psi\rangle=\frac{1}{\sqrt{2}}(\phi_{200}+\phi_{210})$$

Let $E_n^{(2)}=3a_0eE$ then $\alpha=-\beta$

$$\therefore|\psi\rangle=\frac{1}{\sqrt{2}}(\phi_{200}-\phi_{210})$$

$l=1, m=1,0,-1$

$l=0, m=0$



$m=0 \quad \frac{1}{\sqrt{2}}\left(\phi_{200}-\phi_{210}\right)$

$m=\pm 1$

$m=0 \quad \frac{1}{\sqrt{2}}\left(\phi_{200}+\phi_{210}\right)$

2^{nd} order for $l=0$

We have to calculate

$$E_{100}^{(2)}=e^2\varepsilon^2\sum_{k\neq n}\frac{\left|\left\langle\phi_{nlm}\left|z\right|\phi_{100}\right\rangle\right|^2}{E_1^0-E_n^0}$$

$$\begin{aligned}
\left\langle\phi_{nlm}\left|z\right|\phi_{100}\right\rangle &=\int d^3rR_{nlm}\left(r\right)Y_{lm}^*\left(\theta,\phi\right)\cdot r\cos\theta\cdot R_{100}\left(r\right)Y_{00}\left(\theta,\phi\right)\\
&=\int r^2drR_{nlm}\left(r\right)R_{100}\left(r\right)\int d\Omega Y_{lm}^*\left(\theta,\phi\right)\cdot\sqrt{\frac{4\pi}{3}}Y_{10}Y_{00}\\
&=\frac{1}{\sqrt{3}}\delta_{l1}\delta_{m0}\int R_{nlm}\left(r\right)R_{100}\left(r\right)r^2dr\\
&=\frac{1}{\sqrt{3}}\cdot\int_0^\infty R_{n10}\cdot R_{100}\cdot r^2dr \quad \begin{pmatrix} l=1\\ m=0\end{pmatrix}\\
&=\frac{1}{3}\cdot\frac{2^8\cdot n^7\cdot\left(n-1\right)^{2n-5}}{\left(n+1\right)^{2n+5}}a_0^2\\
&=f\left(n\right)a_0^2
\end{aligned}$$

$$\begin{aligned}
E_{100}^{(2)}&=-e^2\varepsilon^2\sum_{nlm}\frac{\left|\left\langle\phi_{nlm}\left|z\right|\phi_{100}\right\rangle\right|^2}{E_1^0-E_n^0}\\
&=-e^2\varepsilon^2a_0^2\sum_{n=2}^\infty\frac{f\left(n\right)\cdot a_0^2}{\frac{1}{2}\mu c^2\alpha^2\left(1-\frac{1}{n^2}\right)}\\
&=-\frac{2e^2\varepsilon^2a_0^2}{\mu c^2\alpha^2}\sum_{n=2}^\infty\frac{n^2f\left(n\right)}{n^2-1}\\
&=-\frac{2\cancel{e}^2\varepsilon^2a_0^2}{\frac{\cancel{e}^2}{a_0}}\sum_{n=2}^\infty\frac{n^2f\left(n\right)}{n^2-1} \quad \left(\mu c^2\cdot\alpha^2=\frac{e^2}{a_0}\right)\\
&=-2\varepsilon^2a_0^3\sum_{n=2}^\infty\frac{n^2f\left(n\right)}{n^2-1}
\end{aligned}$$

$$E_{100}^{(2)}=-2\varepsilon^2a_0^3\sum_{n=2}^\infty\frac{n^2f\left(n\right)}{n^2-1}$$

Induced dipole moment

$$
\begin{aligned}
d &= -\frac{\partial E_{100}^{(2)}}{\partial \varepsilon} \\
&= -4\varepsilon a_0^3 \sum_{n=2}^{\infty} \frac{n^2 f(n)}{n^2 - 1}
\end{aligned}
$$