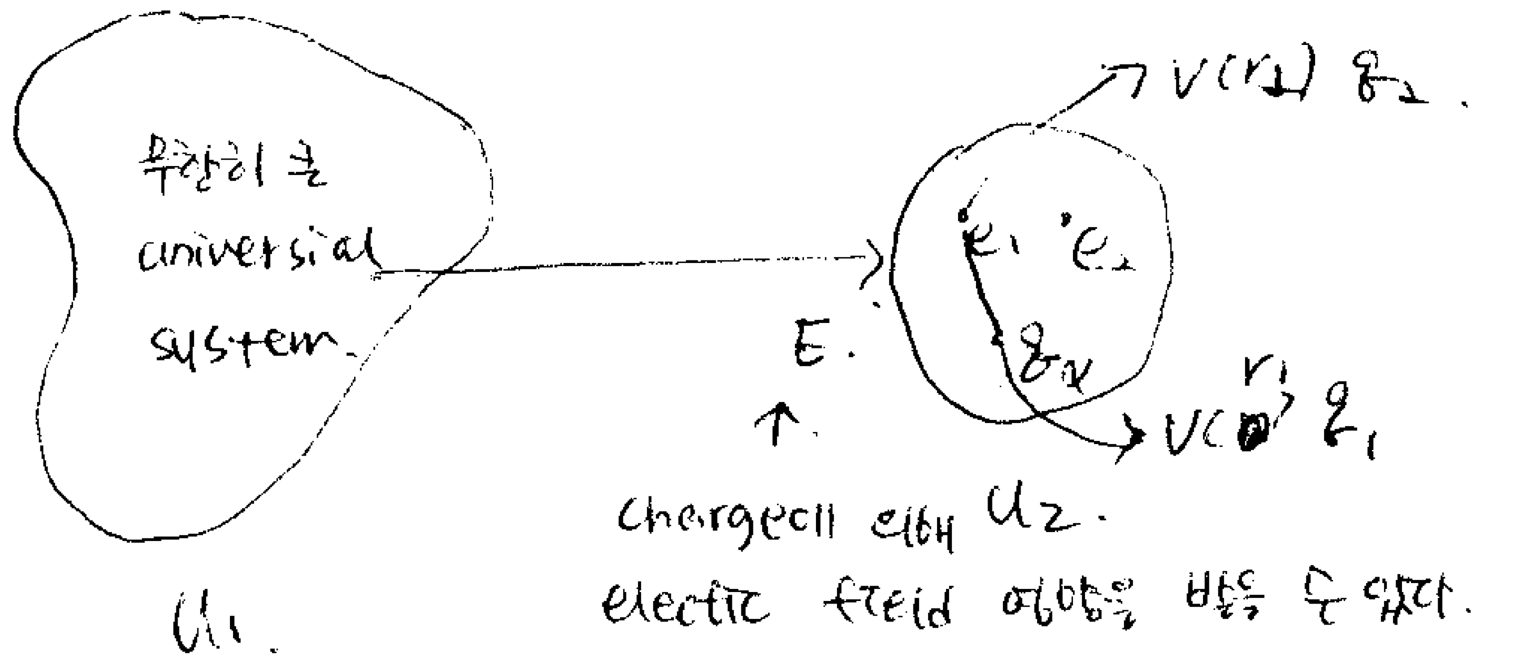


→ 지금까지는 U_1의 영향이 차단되었을 때
U_2만의 배열에 대해서만 계산한 것.
U_1의 영향을 고려시 새로운 Hamitonian 고려.

$$H_0 = \sum_{i=1}^{2}\left(-\frac{\hbar^2}{2m}\nabla_i^2\right) + \sum_i \text{—} + \frac{e^2}{4\pi\varepsilon_0|r_2-r_1|} + \underline{\underline{\text{?}}}$$

만약 U_1의 영향이 많이 작을 경우. 기존의 식을 바꾸지 않고 문제를 해결하는 것이 P.T의 골간!!

→ 위 그림에서 $U = g_\alpha(0) + g_1 V(r_1) + g_2 V(r_2)$

$$= g_\alpha(0) + (-e)V(r_1) + (-e)V(r_2)$$

전자가 2개라면 (He의 경우)

$$2e\,V(0) + (-e)V(r_1) + (-e)V(r_2)$$

$$= [eV(0) + (-e)V(r_1)] + [e\,V(0) + V(r_2)(-e)]$$

$$= -e\big([V(r_1) - V(0)] + [V(r_2) - V(0)]\big)$$

$$\hookrightarrow V(0) + \frac{\partial V}{\partial x}\bigg|_{x=0} r_1 + \cdots = V(0) + \nabla V_{r=0}\cdot\vec{r_1} + \cdots$$

↳ 원점에서의 electric field를 negative 취한것.

$$\left(gV(r_2) = -\int_0^{\vec{r_1}} gE\cdot dr \rightarrow E = -\nabla V \right).$$

$$= -e\left(-\vec{E}(0)\cdot\vec{r_1} - \vec{E}(0)\cdot\vec{r_2} + \cdots\right)$$

$$= -\vec{E}\cdot\sum_{i=1}^{2}(-e)\vec{r_i}$$ → system의 dipole moment $\vec{P}$.

$$= -\underset{U_1}{\vec{E}}\cdot\underset{U_2\ \text{system}}{\vec{P}} = \text{"}V\text{"}$$

새로운 Hamiltonian.

$H = H_0 + V$.

이 solution을 basis set으로 줄 수 있다

$H\Psi = E\Psi \longrightarrow H_0\Phi_I = E_1\Phi_I.\quad H_0\Phi_{II} = E_2\Phi_{II}.$

ϕ_2.
ϕ_1

↑ 정확히 solution을 유한히 2개라 하자.

↳ 따라서 generally

$$\Psi = C_1\Phi_I + C_2\Phi_{II}$$

$$H(C_1\Phi_I + C_2\Phi_{II}) = E(C_1\Phi_I + C_2\Phi_{II}).$$

sol). ① 각각의 Φ를 complex conjugation $= V_{11}$.

$$\langle\Phi_I|H_0|\Phi_{II}\rangle = \overset{E_2}{E_2}\langle\Phi_I|\Phi_{II}\rangle = 0$$

$$\langle\Phi_I|H_0|\Phi_I\rangle + \langle\Phi_I|V|\Phi_I\rangle$$

$$\Rightarrow \begin{pmatrix} \langle\Phi_I|H_0+V|\Phi_I\rangle & \langle\Phi_I|H_0+V|\Phi_{II}\rangle \\ \langle\Phi_{II}|(H_0+V)|\Phi_I\rangle & \langle\Phi_{II}|H_0+V|\Phi_{II}\rangle \end{pmatrix}\begin{pmatrix} C_1 \\ C_2 \end{pmatrix} = E\begin{pmatrix} \underset{1}{\langle\Phi_I|\Phi_I\rangle} & \underset{0}{\langle\Phi_I|\Phi_{II}\rangle} \\ \underset{0}{\langle\Phi_{II}|\Phi_I\rangle} & \underset{1}{\langle\Phi_{II}|\Phi_{II}\rangle} \end{pmatrix}\begin{pmatrix} C_1 \\ C_2 \end{pmatrix}$$

$$\sum_m{}' \sum_n{}' \frac{V_{lm} V_{mn} V_{nl}}{(E_l - E_m)(E_l - E_n)} - V_{ll} \sum_m{}' \frac{V_{lm} V_{ml}}{(E_l - E_m)^2} \cdots$$

지금까지는 CI를 통해 계산한 것 → 다음의 P.T theory를 구하여도 동일한 solution 구할수 있다.

$$H = H_0 + \lambda V$$

$$[H_0 + \lambda V]\Psi = E\Psi$$

$$E \to (E_l + \lambda E_l^{(1)} + \lambda^2 E_l^{(2)} \cdots)$$

$$\Psi \to (\Psi^{(0)} + \lambda \Psi^{(1)} + \lambda^2 \Psi^{(2)} + \cdots)$$

$$\begin{pmatrix} E_1+V_{11}-E & V_{12} \\ V_{21} & E_2+V_{22}-E \end{pmatrix}\begin{pmatrix} c_1 \\ c_2 \end{pmatrix} = -\begin{pmatrix} 0 \\ 0 \end{pmatrix}$$

$$E^{(1)} = \frac{1}{2}\left(E_1+V_{11}+E_2+V_{22} - \sqrt{(E_1-E_2+V_{11}-V_{22})^2 + 4V_{12}V_{21}} \right)$$

$$E^{(2)} = \frac{1}{2}\left(E_1+V_{11}+E_2+V_{22} + \sqrt{(E_1-E_2+V_{11}-V_{22})^2 + 4V_{12}V_{21}} \right)$$

~> potential $V=0$ 일때.

$E^{(1)} = E_2 \qquad E^{(2)} = E_1$ ← CI로 계산했을 때 solution.

$H = H_0 + \lambda V$ 라 하면.

$$E^{(1)} = \frac{1}{2}\left(E_1+\lambda V_{11}+E_2+\lambda V_{22} - \sqrt{(E_1-E_2+\lambda V_{11}-\lambda V_{22})^2 + 4V_{12}V_{21}\lambda^2}\right)$$

$$= \frac{1}{2}\left(E_1+E_2+\lambda V_{11}+\lambda V_{22} - \underbrace{\left|(E_1+E_2+\lambda(V_{11}-V_{22})\right|}_{E_2>E_1\text{이므로}}\left[1+\frac{\lambda^2 4V_{12}V_{21}}{(E_1-E_2+\lambda(V_{11}-V_{22}))^2}\right]^{1/2}\right)$$

$$= \qquad '' \qquad - (E_2-E_1-\lambda(V_{11}-V_{22}))\left[\quad\_\_\_\_\_\quad\right]^{1/2}.$$

$$= E_1 + \lambda V_{11} + \frac{1}{2}$$

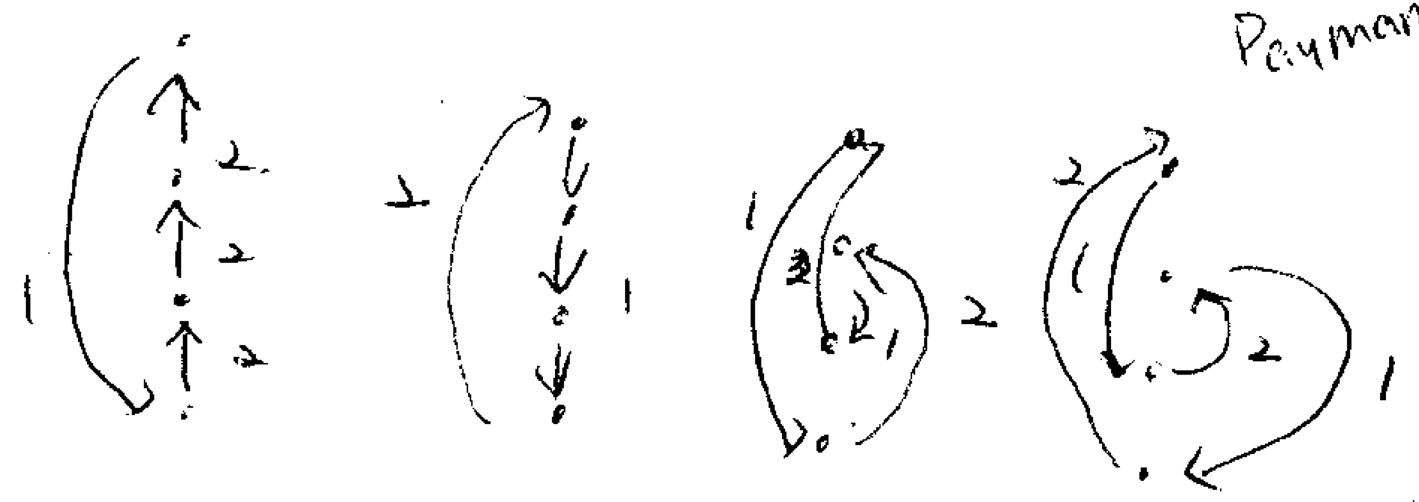
$$E^{(1)} = E_1 + \lambda E_1^{(1)} + \lambda^2 E_1^{(2)} + \lambda^3 E_1^{(3)} + \cdots \quad \frac{V_{12}V_{22}V_{21}}{(E_1-E_2)^2} - \frac{V_{12}V_{21}V_{11}}{(E_1-E_2)^2}.$$

$E_1^{(1)} \to V_{11} = \langle\Phi_1|V|\Phi_1\rangle.$

$E_1^{(2)} \to \dfrac{V_{12}V_{21}}{E_1-E_2}$, 2.

$$\cdots + \lambda^4 E_1^{(4)}$$

Paymann - diagram.



→ hole (1을 counting 해야..)

→ 부호결정 $(-1)^{h+l}$

$$\frac{V_{12}V_{22}V_{22}V_{21}}{(E_1-E_2)^3} + \frac{V_{21}V_{11}V_{11}V_{12}}{(E_1-E_2)^3} - \frac{V_{21}V_{11}V_{11}V_{12}}{(E_1-E_2)^2} - \frac{V_{21}V_{12}V_{21}V_{12}}{(E_1-E_2)^2(2E_1-2E_2)}$$

E_l

E_2

E_1

→ 내려오는 P.T를 우리가 관심있어하는 l번째 state가 지배하자.

l, n, m

$$E_l = E_l + \lambda E_l^{(1)} + \lambda^2 E_l^{(2)} + \cdots$$

$E_l^{(1)} \to V_{ll}$.

$$E_l^{(2)} \to \sum_m \frac{V_{lm}V_{ml}}{E_l - E_m}$$

l, n, m, l 로 두게