§2準位系の摂動論(非縮退)

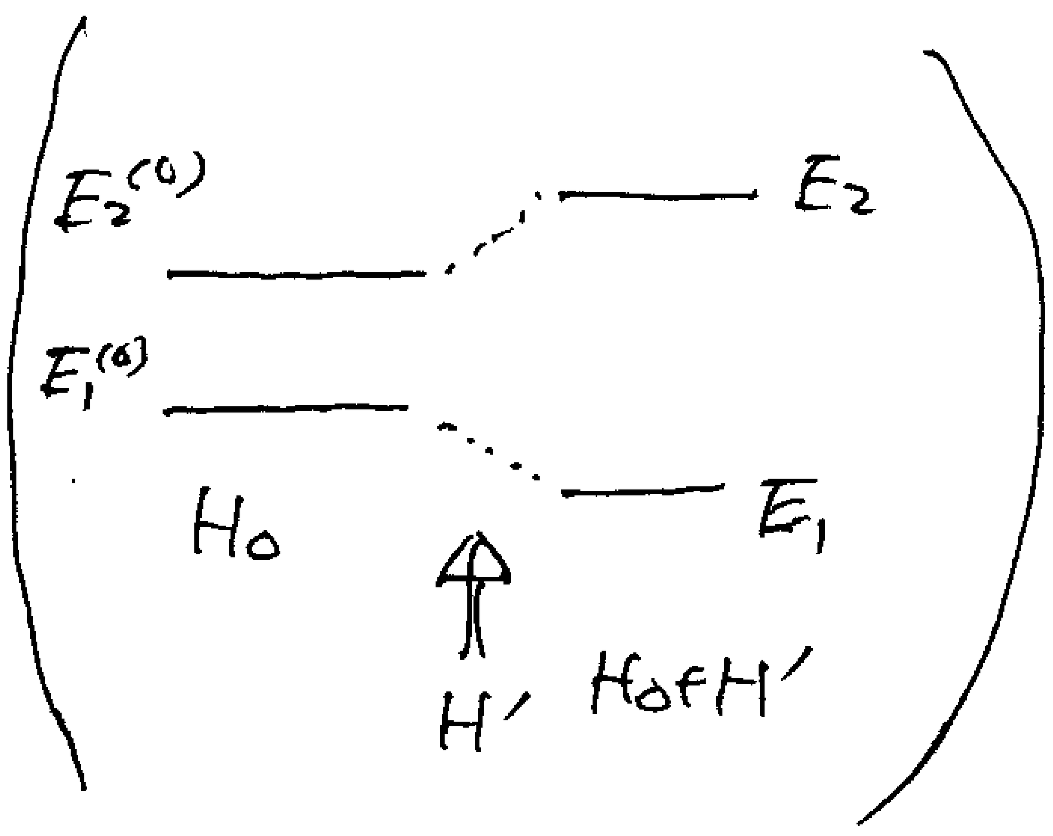
無摂動系

$$H_0 \psi_n^{(0)} = E_n^{(0)} \psi_n^{(0)} \quad \cdots (1) \qquad (n=1,2)$$

$$\begin{cases} \int_{-\infty}^{\infty} \psi_n^{(0)*}(x) \cdot \psi_m^{(0)}(x)\, dx = \delta_{nm} & (2.1) \quad (n, m = 1, 2) \\ E_1^{(0)} \neq E_2^{(0)} \ (\text{非縮退}) & (2.2) \end{cases}$$

摂動系

$$\boxed{\begin{aligned} & H = H_0 + H' && (3) \\ & H \psi_n = E_n \cdot \psi_n && (4) \\ & \psi_n = C_{n1} \cdot \psi_1^{(0)} + C_{n2} \psi_2^{(0)} && (5) \end{aligned}}$$



逐次近似法 (H'の次数についての展開)

$$\boxed{\begin{aligned} & E_n = E_n^{(0)} + E_1^{(1)} + E_2^{(2)} + \cdots && (6) \\ & C_{nm} = C_{nm}^{(0)} + C_{nm}^{(1)} + C_{nm}^{(2)} + \cdots && (7) \\ & C_{nm}^{(0)} = \delta_{nm} && (8) \end{aligned}}$$

(5)を(4)に代入して

$$(H_0 + H')(C_{n1}\psi_1^{(0)} + C_{n2}\psi_2^{(0)}) = E_n (C_{n1}\psi_1^{(0)} + C_{n2}\psi_2^{(0)}) \quad (9)$$

$\psi_m^{(0)*}$を:かけてxについて積分

$$\int_{-\infty}^{\infty} \psi_m^{(0)*} (H_0 + H')(C_{n1}\psi_1^{(0)} + C_{n2}\psi_2^{(0)})\, dx = E_n \int \psi_m^{(0)*} (C_{n1} \cdot \psi_1^{(0)} + C_{n2}\psi_2^{(0)})\, dx$$

$$\rightarrow (C_{n1} \cdot E_1^{(0)} \cdot \delta_{m1} + C_{n2} \cdot E_2^{(0)} \cdot \delta_{m2}) + C_{n1} \cdot H'_{m1} + C_{n2} H'_{m2}$$

$$= E_n \cdot (C_{n1} \cdot \delta_{m1} + C_{n2} \cdot \delta_{m2})$$

$$\therefore \boxed{\begin{aligned} & (E_m^{(0)} - E_n) \cdot C_{nm} = -(C_{n1} H'_{m1} + C_{n2} H'_{m2}) && (10)\ (\text{exact}) \\ & H'_{mn} \equiv \int_{-\infty}^{\infty} \psi_m^{(0)*} H' \psi_n^{(0)}\, dx, && (11)\ (11.1) \end{aligned}}$$

$$\boxed{H'_{mn} = H'^{*}_{nm} \quad (\text{ハミルトニアンのエルミート性})} \quad (11.2)$$

1次の摂動（H'の1次まで考慮する）

$$\left.\begin{aligned} E_n &\simeq E_n^{(0)} + E_n^{(1)} && (12.1) \\ C_{nm} &\cong C_{nm}^{(0)} + C_{nm}^{(1)} \\ &= \delta_{nm} + C_{nm}^{(1)} && (12.2) \end{aligned}\right\}$$

(12)を(10)に代入

$$\left(E_m^{(0)} - E_n^{(0)} - E_n^{(1)}\right)\left(\delta_{nm} + C_{nm}^{(1)}\right) \fallingdotseq -\left(\delta_{n1} + C_{n1}^{(1)}\right)H'_{m1} - \left(\delta_{n2} + C_{n2}^{(1)}\right)H'_{m2} \quad (13$$

ここで $m=n$ のとき（$m=n=1$ or $m=n=2$）：

(13)において H'の1次までを考えると

$$-E_n^{(1)} \fallingdotseq -H'_{nn}$$

$$\therefore \boxed{E_n^{(1)} = H'_{nn} \ \text{or} \ E_1^{(1)} = H'_{11},\ E_2^{(1)} = H'_{22}} \quad (13)$$

さらに $m \neq n$ のとき（$m=1, n=2$ or $m=2, n=1$）

$$\left(E_m^{(0)} - E_n^{(0)}\right) \cdot C_{nm}^{(1)} \fallingdotseq -H'_{mn}$$

$$\therefore \boxed{\underset{(n \neq m)}{C_{nm}^{(1)}} = \frac{H'_{mn}}{E_n^{(0)} - E_m^{(0)}} \ \text{or} \ C_{12}^{(1)} = \frac{H'_{21}}{E_1^{(0)} - E_2^{(0)}},\ C_{21}^{(1)} = \frac{H'_{12}}{E_2^{(0)} - E_1^{(0)}}} \quad (14)$$

◎ $C_{nn}^{(1)}$の決定

$$\psi_1 \simeq C_{11} \cdot \psi_1^{(0)} + C_{12}\psi_2^{(0)}$$

$$\cong \left(1 + C_{11}^{(1)}\right)\psi_1^{(0)} + C_{12}^{(1)}\psi_2^{(0)}$$

$$1 = \int_{-\infty}^{\infty} \psi_1^{*} \cdot \psi_1 \, dx$$

$$\fallingdotseq \left|1 + C_{11}^{(1)}\right|^2 + \left|C_{12}^{(1)}\right|^2$$

$$\cong 1 + C_{11}^{(1)} + C_{11}^{(1)*} \quad ($$

$$\therefore \ C_{11}^{(1)} + C_{11}^{(1)*} = 0$$ ：$C_{11}^{(1)}$は純虚数

ここで

$$1 + C_{11}^{(1)} = 1 + i|C_{11}^{(1)}|$$
$$\cong \exp(i|C_{11}^{(1)}|)$$

$$\Psi_1 \cong \underbrace{\exp(i|C_{11}^{(1)}|)\cdot\Psi_1^{(0)}}_{\equiv \Psi_1^{(0)\prime}} + \cdots C_{12}^{(1)}\Psi_2^{(0)}$$

$\equiv \Psi_1^{(0)\prime}$ とおくと

$$|\Psi_1^{(0)}|^2 = |\Psi_1^{(0)\prime}|^2$$

$$\boxed{C_{nn}^{(1)} \equiv 0} \quad (15)$$

位相はゼロとおける！ $\boxed{C_{11}^{(1)} \equiv 0}$ (15.1)

同様に $\boxed{C_{22}^{(1)} = 0}$ (15.2)

$$\therefore \boxed{\begin{aligned}\Psi_1 &\cong \Psi_1^{(0)} + C_{12}^{(1)}\Psi_2^{(0)} \\ &= \Psi_1^{(0)} + \underbrace{\left(\frac{H'_{21}}{E_1^{(0)} - E_2^{(0)}}\right)}_{\text{摂動による混合係数}}\cdot\Psi_2^{(0)}\end{aligned}} \quad (16)$$

・2次の摂動

$$E_n \cong E_n^{(0)} + E_n^{(1)} + E_2^{(2)} \qquad (17)$$

$$C_{nm} \cong \delta_{nm} + C_{nm}^{(1)} + C_{nm}^{(2)} \qquad (18)$$

(17), (18) を(10)に代入して H' について2次の項までを考慮する。

$$\left(E_m^{(0)} - E_n^{(0)} - E_n^{(1)} - E_n^{(2)}\right)\left(\delta_{nm} + C_{nm}^{(1)} + C_{nm}^{(2)}\right)$$
$$\cong -\left[(\delta_{n1} + C_{n1}^{(1)}) H'_{m1} + (\delta_{n2} + C_{n2}^{(1)}) H'_{m2} \right] \qquad (19)$$

$n = m$ (=1) の場合：(19) と(15) より

$$\left(-E_1^{(1)} - E_1^{(2)}\right)$$
$$\cong -H'_{11} + C_{12}^{(1)} \cdot H'_{12}$$

(16) を用いると

$$\boxed{E_1^{(2)} = \frac{|H'_{12}|^2}{E_1^{(0)} - E_2^{(0)}}} \qquad (20.1)$$

同様にして

$$\boxed{E_2^{(2)} = \frac{|H'_{21}|^2}{E_2^{(0)} - E_1^{(0)}} \left(= -\frac{|H'_{12}|^2}{E_1^{(0)} - E_2^{(0)}} = -E_1^{(2)} \right)} \qquad (20.2)$$

$\therefore\ E_1^{(2)} + E_2^{(2)} = 0$

(第2,3の等号は2準位系の特徴)

$n \neq m$ ($n=1, m=2$) の場合：(19) と(15) より

$$\left(E_2^{(0)} - E_1^{(0)} - E_1^{(1)} - E_1^{(2)}\right)\left(C_{12}^{(1)} + C_{12}^{(2)}\right)$$
$$\cong -\left[H'_{21} + C_{12}^{(1)} \cdot H'_{22} \right]$$

$$\rightarrow \left(E_2^{(0)} - E_1^{(0)}\right) \cdot C_{12}^{(1)} + \left(E_2^{(0)} - E_1^{(0)}\right) C_{12}^{(2)} - E_1^{(1)} \cdot C_{12}^{(1)}$$
$$= -H'_{21} - C_{12}^{(1)} \cdot H'_{22}$$

$$\boxed{C_{12}^{(2)} = \frac{H'_{21}\cdot H'_{22}}{(E_1^{(0)}-E_2^{(0)})^2} - \frac{H'_{11}\cdot H'_{21}}{(E_1^{(0)}-E_2^{(0)})^2}} \quad (21) //$$

同様にして

$$\boxed{C_{21}^{(2)} = \frac{H'_{12}\cdot H'_{11}}{(E_2^{(0)}-E_1^{(0)})^2} - \frac{H'_{22}\cdot H'_{12}}{(E_2^{(0)}-E_1^{(0)})^2}} \quad (22) //$$

$C_{nn}^{(2)}$の決定；波動関数をH'の2次の項まで考慮すると

$$\psi_n = C_{n1}\cdot\psi_1^{(0)} + C_{n2}\cdot\psi_2^{(0)}$$
$$= (\delta_{n1} + C_{n1}^{(1)} + C_{n1}^{(2)})\psi_1^{(0)} + (\delta_{n2} + C_{n2}^{(1)} + C_{n2}^{(2)})\psi_2^{(0)} \quad (23)$$

$n=1$；(15)を用いて

$$\psi_1 = (1 + C_{11}^{(2)})\psi_1^{(0)} + (C_{12}^{(1)} + C_{12}^{(2)})\cdot\psi_2^{(0)} \quad (24)$$

ここで波動関数の規格化を行う。(2.1)を用いて

$$1 = \int_{-\infty}^{\infty}\psi_1^*(x)\cdot\psi_1(x)dx$$
$$= |1 + C_{11}^{(2)}|^2 + |C_{12}^{(1)} + C_{12}^{(2)}|^2$$
$$\fallingdotseq 1 + C_{11}^{(2)} + C_{11}^{(2)*} + |C_{12}^{(1)}|^2 \quad (25)$$

ここで

$$C_{11}^{(2)} = a + ib \quad (a, b：実数) \quad (26)$$

とおくと(25)より

$$2a + |C_{12}^{(1)}|^2 = 0$$

$$\therefore \quad a = -\frac{|C_{12}^{(1)}|^2}{2} \quad (27)$$

(27)を(24)に代入すると

$$\psi_1 = (1 + a + ib)\psi_1^{(0)} + (C_{12}^{(1)} + C_{12}^{(2)})\cdot\psi_2^{(0)} \quad (28)$$

$C_{11}^{(1)}$の決定の場合と同様の理由で　$b=0$とおいてよい。

$$\boxed{C_{11}^{(2)} = -\frac{1}{2}\frac{|H'_{12}|^2}{(E_1^{(0)}-E_2^{(0)})^2}} \quad (28)$$

$$C_{22}^{(2)} = -\frac{1}{2}\frac{|H'_{21}|^2}{(E_2^{(0)}-E_1^{(0)})^2} = C_{11}^{(2)} \quad (29)$$

波動関数を H'の行列要素を用いて表わすと

$$\psi_1 = \psi_1^{(0)} + \left(\frac{H'_{21}}{E_1^{(0)}-E_2^{(0)}}\right)\psi_2^{(0)} - \frac{1}{2}\frac{|H'_{12}|^2}{(E_1^{(0)}-E_2^{(0)})^2}\psi_1^{(0)} + \left[\frac{H'_{21}\cdot H'_{22}}{(E_1^{(0)}-E_2^{(0)})^2} - \frac{H'_{11}\cdot H'_{21}}{(E_1^{(0)}-E_2^{(0)})}\right]\psi_2^{(0)} \quad (30)$$

$$\psi_2 = \psi_2^{(0)} + \left(\frac{H'_{12}}{E_2^{(0)}-E_1^{(0)}}\right)\psi_1^{(0)} - \frac{1}{2}\frac{|H'_{21}|^2}{(E_2^{(0)}-E_1^{(0)})^2}\psi_2^{(0)} + \left[\frac{H'_{12}\cdot H'_{11}}{(E_2^{(0)}-E_1^{(0)})^2} - \frac{H'_{22}\cdot H'_{12}}{(E_2^{(0)}-E_1^{(0)})^2}\right]\psi_1^{(0)} \quad (31)$$