非線形感受率　ダイアグラムによる解法

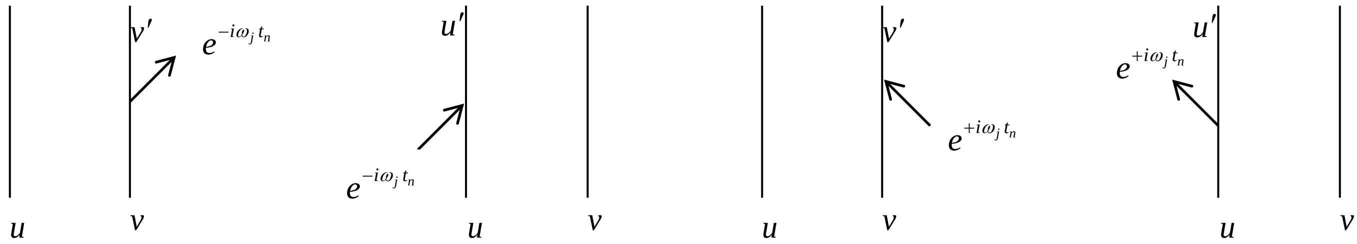
$$\frac{d}{dt}\rho_{12}+i\omega_{12}\rho_{12}+\gamma_2\rho_{12}=i\eta_{12}(\rho_{22}-\rho_{11}) \qquad \frac{d}{dt}\rho_{21}+i\omega_{21}\rho_{21}+\gamma_2\rho_{21}=-i\eta_{21}(\rho_{22}-\rho_{11})$$

$$\frac{d}{dt}\rho_{22}+\gamma_1\rho_{22}=i(\eta_{21}\rho_{12}-\eta_{12}\rho_{21})$$

$$\omega_{12}=\omega_1-\omega_2$$

$$\rho_{12}^{(1)}(t)=e^{-i\omega_{12}t-\gamma_2 t}\int_{-\infty}^{t}dt'[i\eta_{12}(\rho_{22}^{(0)}-\rho_{11}^{(0)})]e^{+i\omega_{12}t'+\gamma_2 t'}=\int_{-\infty}^{t}dt_1[i\frac{\mu_{12}E_0}{2\hbar}(e^{i\omega t_1}+e^{-i\omega t_1})(\rho_{22}^{(0)}-\rho_{11}^{(0)})]e^{-i\omega_{12}(t-t_1)-\gamma_2(t-t_1)}$$

$$\rho_{22}^{(2)}(t)=e^{-\gamma_1 t}\int_{-\infty}^{t}dt'[i(\eta_{21}\rho_{12}^{(1)}-\eta_{12}\rho_{21}^{(1)})]e^{+\gamma_1 t'}=\int_{-\infty}^{t}dt_2[i\frac{\mu_{21}E_0}{2\hbar}(e^{-i\omega t_2}+e^{i\omega t_2})\rho_{12}^{(1)}(t_2)-i\frac{\mu_{12}E_0}{2\hbar}(e^{i\omega t_2}+e^{-i\omega t_2})\rho_{21}^{(1)}(t_2)]e^{-\gamma_1(t-t_2)}$$



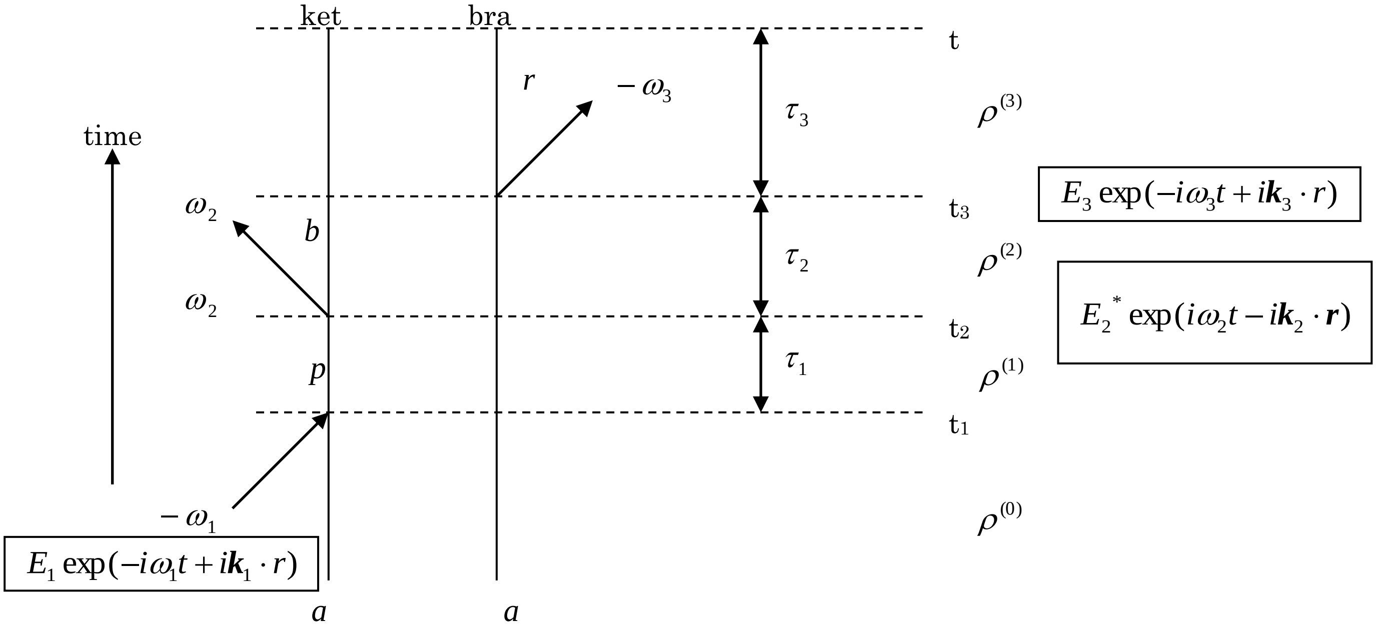
$$\left.\begin{aligned}\rho_{uv'}^{(n)}(t_n)&=\frac{-i\mu_{vv'}E(\pm\omega_j)}{2\hbar}e^{\mp i\omega_j t_n}\rho_{uv}^{(n-1)}(t_n)\\ \rho_{u'v}^{(n)}(t_n)&=\frac{+i\mu_{u'u}E(\pm\omega_j)}{2\hbar}e^{\mp i\omega_j t_n}\rho_{uv}^{(n-1)}(t_n)\end{aligned}\right\}\text{遷移}$$

$E(t)=E_0^0\cos(\omega t+\varphi)$のとき　$E_0\equiv E_0^0 e^{-i\varphi}$

$$E(t)=\frac{E_0(\omega)}{2}e^{-i\omega t}+\frac{E_0^{\ *}(\omega)}{2}e^{i\omega t} \qquad E_0^{\ *}(\omega)=E_0(-\omega)$$

$$\rho_{uv'}^{(n)}(t;t_n)=\frac{-i\mu_{vv'}E(\pm\omega_j)}{2\hbar}e^{\mp i\omega_j t_n}\rho_{uv}^{(n-1)}(t_n;t_{n-1})e^{-i\omega_{uv'}(t-t_n)-\gamma_{uv'}(t-t_n)}$$ 時間発展　$t_n\to t$

$$\rho_{ij}=C_iC_j^{\ *}$$



$$\rho_{pa}^{(1)}(t;t_1)=\frac{i\mu_{pa}E(\omega_1)}{2\hbar}e^{-i\omega_1 t_1}e^{-i(\omega_{pa}-i\gamma_{pa})(t-t_1)}\rho_{aa}^{(0)}(t_1)$$
$$\rho_{ba}^{(2)}(t;t_1,t_2)=\frac{i\mu_{bp}E(-\omega_2)}{2\hbar}e^{i\omega_2 t_2}e^{-i(\omega_{ba}-i\gamma_{ba})(t-t_2)}\rho_{pa}^{(1)}(t_2;t_1)$$
$$\rho_{br}^{(3)}(t;t_1,t_2,t_3)=\frac{-i\mu_{ar}E(\omega_3)}{2\hbar}e^{-i\omega_3 t_3}e^{-i(\omega_{br}-i\gamma_{br})(t-t_3)}\rho_{ba}^{(2)}(t_3;t_2,t_1)$$
$$\tau_n=t_{n+1}-t_n \qquad \tau_3=t-t_3 \quad \tau_2=t_3-t_2 \quad \tau_1=t_2-t_1$$
$$t_3=t-\tau_3 \quad t_2=t_3-\tau_2=t-\tau_3-\tau_2 \quad t_1=t_2-\tau_1=t-\tau_3-\tau_2-\tau_1$$
$$dt_3=-d\tau_3 \quad dt_2=-d\tau_2 \quad dt_1=-d\tau_1$$
$$\rho_{br}^{(3)}(t)=\int_{-\infty}^{t}dt_3\int_{-\infty}^{t_3}dt_2\int_{-\infty}^{t_2}dt_1\rho_{br}^{(3)}(t;t_1,t_2,t_3)$$
$$=\iiint dt_3 dt_2 dt_1$$
$$\frac{[-i\mu_{ar}E(\omega_3)][i\mu_{bp}E(-\omega_2)][i\mu_{pa}E(\omega_1)]}{8\hbar^3}e^{-i\omega_3 t_3+i\omega_2 t_2-i\omega_1 t_1}e^{-i(\omega_{br}-i\gamma_{br})(t-t_3)-i(\omega_{ba}-i\gamma_{ba})(t_3-t_2)-i(\omega_{pa}-i\gamma_{pa})(t_2-t_1)}\rho_{aa}^{(0)}(t_1)$$
$$=\frac{[\,][\,][\,]}{8\hbar^3}\int_0^\infty d\tau_3\int_0^\infty d\tau_2\int_0^\infty d\tau_1 e^{-i\omega_3(t-\tau_3)+i\omega_2(t-\tau_3-\tau_2)-i\omega_1(t-\tau_3-\tau_2-\tau_1)}e^{-i(\omega_{br}-i\gamma_{br})\tau_3-i(\omega_{ba}-i\gamma_{ba})\tau_2-i(\omega_{pa}-i\gamma_{pa})\tau_1}\rho_{aa}^{(0)}(t_1)$$
$$=\frac{[\,][\,][\,]}{8\hbar^3}e^{-i(\omega_3-\omega_2+\omega_1)t}\iiint d\tau_3 d\tau_2 d\tau_1 e^{-i(\omega_{br}-\omega_3+\omega_2-\omega_1-i\gamma_{br})\tau_3-i(\omega_{ba}+\omega_2-\omega_1-i\gamma_{ba})\tau_2-i(\omega_{pa}-\omega_1-i\gamma_{pa})\tau_1}\rho_{aa}^{(0)}(t_1)$$
$$=\frac{[\,][\,][\,]}{8\hbar^3}e^{-i(\omega_3-\omega_2+\omega_1)t}\frac{-1}{-i(\omega_{br}-\omega_3+\omega_2-\omega_1-i\gamma_{br})}\frac{-1}{-i(\omega_{ba}+\omega_2-\omega_1-i\gamma_{ba})}\frac{-1}{-i(\omega_{pa}-\omega_1-i\gamma_{pa})}\rho_{aa}^{(0)}$$
$$=\frac{-\mu_{ar}\mu_{bp}\mu_{pa}E(\omega_3)E(-\omega_2)E(\omega_1)}{8\hbar^3}e^{-i(\omega_3-\omega_2+\omega_1)t}\frac{1}{(\omega_{br}-\omega_3+\omega_2-\omega_1-i\gamma_{br})}\frac{1}{(\omega_{ba}+\omega_2-\omega_1-i\gamma_{ba})}\frac{1}{(\omega_{pa}-\omega_1-i\gamma_{pa})}\rho_{aa}^{(0)}$$
$$P=\frac{N}{V}\mathrm{Tr}(\rho\mu)=\frac{N}{V}\sum_r\rho_{br}\mu_{rb}=\frac{N}{V}\sum_b\mu_{rb}\rho_{br}$$
$$\mu_{ar}\mu_{rb}\mu_{bp}\mu_{pa}$$
$$P_k^{(3)}(\omega_3-\omega_2+\omega_1)=\varepsilon_0\chi_{klmn}^{(3)}(\omega_3-\omega_2+\omega_1;-\omega_3,+\omega_2,-\omega_1)(\frac{E_l(\omega_3)}{2}e^{-i\omega_3 t})(\frac{E_m(-\omega_2)}{2}e^{+i\omega_2 t})(\frac{E_n(\omega_1)}{2}e^{-i\omega_1 t})$$
$$\chi_{klmn}^{(3)}(\omega_3-\omega_2+\omega_1;-\omega_3,+\omega_2,-\omega_1)=\frac{N}{V\varepsilon_0}\frac{(-1)}{\hbar^3}\sum_{arbp}\mu_{ar}^l\mu_{rb}^k\mu_{bp}^m\mu_{pa}^n\frac{1}{(\omega_{br}-\omega_3+\omega_2-\omega_1-i\gamma_{br})}\frac{1}{(\omega_{ba}+\omega_2-\omega_1-i\gamma_{ba})}\frac{1}{(\omega_{pa}-\omega_1-i\gamma_{pa})}\rho_{aa}^{(0)}$$

$$\mathrm{Tr}(\rho\mu)=\mathrm{Tr}\left[\begin{pmatrix}\rho_{11}&\rho_{12}&\rho_{13}\\\rho_{21}&\rho_{22}&\rho_{23}\\\rho_{31}&\rho_{32}&\rho_{33}\end{pmatrix}\begin{pmatrix}\mu_{11}&\mu_{12}&\mu_{13}\\\mu_{21}&\mu_{22}&\mu_{23}\\\mu_{31}&\mu_{32}&\mu_{33}\end{pmatrix}\right]$$
$$=(\rho_{11}\mu_{11}+\rho_{12}\mu_{21}+\rho_{13}\mu_{31})+(\rho_{21}\mu_{12}+\rho_{22}\mu_{22}+\rho_{23}\mu_{32})+(\rho_{31}\mu_{13}+\rho_{32}\mu_{23}+\rho_{33}\mu_{33})=\sum_b(\sum_r\rho_{br}\mu_{rb})=\sum_b(\sum_r\mu_{rb}\rho_{br})$$
$$=(\rho_{11}\mu_{11}+\rho_{21}\mu_{12}+\rho_{31}\mu_{13})+(\rho_{12}\mu_{21}+\rho_{22}\mu_{22}+\rho_{32}\mu_{23})+(\rho_{13}\mu_{31}+\rho_{23}\mu_{32}+\rho_{33}\mu_{33})=\sum_r(\sum_b\rho_{br}\mu_{rb})$$

$$a=1, b=1, p=2, r=2 \quad \omega_3=\omega_2=\omega_1=\omega$$

$$\chi^{(3)}_{klmn}(\omega;-\omega,+\omega,-\omega)=\frac{N}{V\varepsilon_0}\frac{(-1)}{\hbar^3}\sum_{arbp}\mu^l_{12}\mu^k_{21}\mu^m_{12}\mu^n_{21}\frac{1}{(\omega_{12}-\omega-i\gamma_{12})}\frac{1}{(\omega_{11}-i\gamma_{11})}\frac{1}{(\omega_{21}-\omega-i\gamma_{21})}\rho^{(0)}_{11}$$