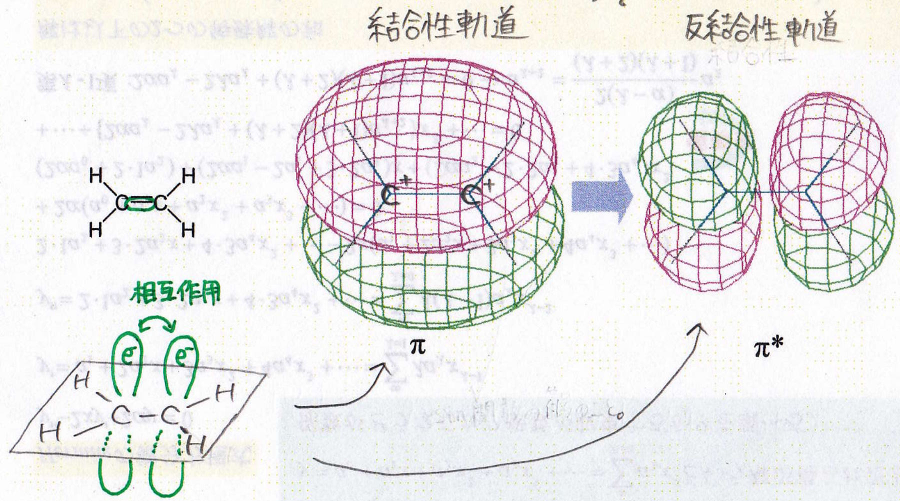
プリントNO.5

sin 関数が +と+

→合成して大きくなる→がっちりくっつく。




## 三次元の箱の中の粒子(箱の3辺の長さa,b,c):式誘導

箱の中: $V_x = V_y = V_z = 0$, 箱の外: $V_x = V_y = V_z = \infty$

$$\left[-\frac{\hbar^2}{2m}\left(\frac{\partial^2}{\partial x^2}+\frac{\partial^2}{\partial y^2}+\frac{\partial^2}{\partial z^2}\right)+V\right]\phi = E\phi$$

変数分離

変数分離①
$\phi(x,y,z) = X(x)Y(y)Z(z)$

$$-\frac{\hbar^2}{2m}\left(Y(y)Z(z)\frac{\partial^2 X(x)}{\partial x^2}+X(x)Z(z)\frac{\partial^2 Y(y)}{\partial y^2}+X(x)Y(y)\frac{\partial^2 Z(z)}{\partial z^2}\right)+VX(x)Y(y)Z(z) = EX(x)Y(y)Z(z)$$

変数分離

$$\frac{\partial^2 X(x)}{\partial x^2}+\frac{2m}{\hbar^2}(E_x - V_x)X(x) = 0$$

$$\frac{\partial^2 Y(y)}{\partial y^2}+\frac{2m}{\hbar^2}(E_y - V_y)Y(y) = 0$$

$$\frac{\partial^2 Z(z)}{\partial z^2}+\frac{2m}{\hbar^2}(E_z - V_z)Z(z) = 0$$

$$E = E_x + E_y + E_z$$

$$\phi_{nxnynz} = \sqrt{\frac{8}{abc}}\sin\frac{n_x\pi}{a}x\sin\frac{n_y\pi}{b}y\sin\frac{n_z\pi}{c}z$$

$$E_{nxnynz} = \frac{\pi^2\hbar^2}{2m}\left(\frac{n_x^{\ 2}}{a^2}+\frac{n_y^{\ 2}}{b^2}+\frac{n_z^{\ 2}}{c^2}\right)$$

$n_x, n_y, n_z = 1,2,3\cdots$

変数分離②

左辺がx、yだけの関数、右辺がzだけの関数

それぞれが定数でなければならない→ $\frac{2m}{\hbar^2}E_z$とおく

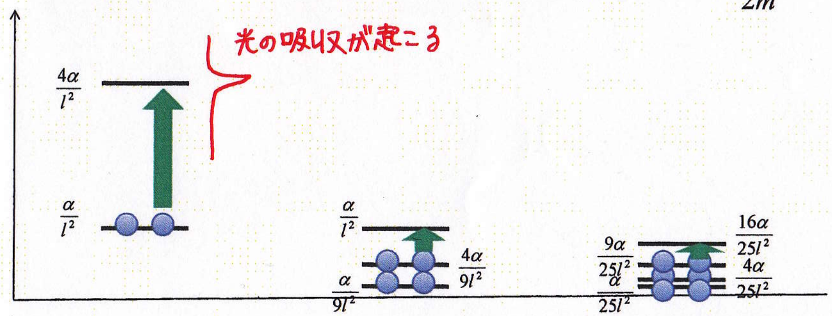
$$\frac{\partial^2 Z(z)}{\partial z^2}+\frac{2m}{\hbar^2}(E_z - V_z)Z(z) = 0$$

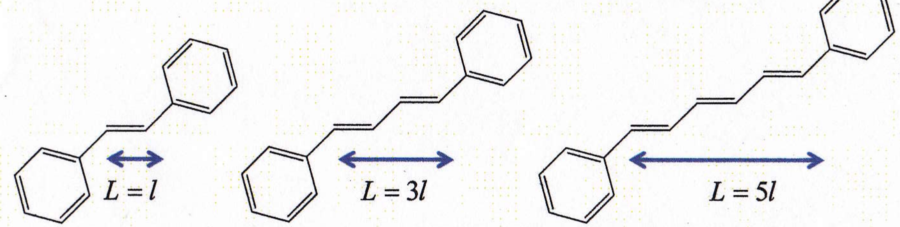
$$\frac{1}{X(x)}\frac{\partial^2 X(x)}{\partial x^2}+\frac{1}{Y(y)}\frac{\partial^2 Y(y)}{\partial y^2}+\frac{2m}{\hbar^2}(E - V_x - V_y) = \frac{2m}{\hbar^2}E_z$$

上式をx、yについて同様の操作

## 教科書5
## ジフェニルポリエンの鎖長、色、吸収波長

$$\alpha = \frac{\pi^2\hbar^2}{2m}$$




## 三次元の箱の中の粒子(立方体:3辺の長さ全てa):式誘導

$$\phi_{nxnynz} = \sqrt{\frac{8}{a^3}}\sin\frac{n_x\pi}{a}x\sin\frac{n_y\pi}{a}y\sin\frac{n_z\pi}{a}z$$

$$E_{nxnynz} = \frac{\pi^2\hbar^2}{2ma^2}\left(n_x^{\ 2}+n_y^{\ 2}+n_z^{\ 2}\right)$$

| $(n_x, n_y, n_z)$ | $E_{nxnynz}$ |
|---|---|
| (1,1,1) | $\frac{3\pi^2\hbar^2}{2ma^2}$ |
| (1,1,2) | $\frac{6\pi^2\hbar^2}{2ma^2}$ |
| (1,2,1) | $\frac{6\pi^2\hbar^2}{2ma^2}$ |
| (2,1,1) | $\frac{6\pi^2\hbar^2}{2ma^2}$ |
| (1,2,2) | $\frac{9\pi^2\hbar^2}{2ma^2}$ |
| (2,1,2) | $\frac{9\pi^2\hbar^2}{2ma^2}$ |
| (2,2,1) | $\frac{9\pi^2\hbar^2}{2ma^2}$ |

エネルギーが一緒の状態が幾つかある
→縮重・縮退

調和振動子の式の誘導

$$\frac{\partial^2\phi}{\partial x^2}+(\varepsilon-\beta^2x^2)\phi=0\left(\varepsilon=\frac{8\pi^2mE}{h^2},\beta=\frac{2\pi m\omega}{h}\right)$$

$\varepsilon << \beta^2x^2$

$x$が非常に大きい時の近似解

$\phi''=\beta^2x^2\{c_1\exp(\beta x^2/2)+c_2\exp(-\beta x^2/2)\}+\beta\{c_1\exp(\beta x^2/2)-c_2\exp(-\beta x^2/2)\}$

なので$\beta^2x^2>>\beta$の時、$\frac{\partial^2\phi}{\partial x^2}=\beta^2x^2\phi$を満たす

$$\frac{\partial^2\phi}{\partial x^2}=\beta^2x^2\phi$$

$$\phi=c_1\exp(\beta x^2/2)+c_2\exp(-\beta x^2/2)$$

$c$を$f(x)$として漸近関数として使う

$|x|\to\infty$において$\phi\to 0$

$$\phi=f(x)\exp(-\beta x^2/2)$$

$$\frac{\partial\phi}{\partial x}=-\beta xf(x)\exp(-\beta x^2/2)+f'(x)\exp(-\beta x^2/2)$$

$$\frac{\partial^2\phi}{\partial x^2}=\beta^2x^2f(x)\exp(-\beta x^2/2)-\beta f(x)\exp(-\beta x^2/2)-2\beta xf'(x)\exp(-\beta x^2/2)+f''(x)\exp(-\beta x^2/2)$$

$$\frac{\partial^2\phi}{\partial x^2}+(\varepsilon-\beta^2x^2)\phi=0$$

$$\beta^2x^2f(x)\exp(-\beta x^2/2)-\beta f(x)\exp(-\beta x^2/2)-2\beta xf'(x)\exp(-\beta x^2/2)$$
$$+f''(x)\exp(-\beta x^2/2)+(\varepsilon-\beta^2x^2)f(x)\exp(-\beta x^2/2)=0$$
$$f''(x)-2\beta xf'(x)+(\varepsilon-\beta)f(x)=0$$

級数による解法：まともにぶつかって解けない

$y=a_0+a_1x+a_2x^2+a_3x^3+\cdots=\sum_{\lambda=0}^{\infty}a_\lambda x^\lambda$という解が得られたとして

係数がどうなるか？級数が収束するか？を調べる。

*Hermite*の微分方程式

$$y''-2xy'+2\alpha y=0$$

$$y'=a_1+2a_2x+3a_3x^2+4a_4x^3+\cdots=\sum_{\lambda=1}^{\infty}\lambda a_\lambda x^{\lambda-1}$$

$$y''=2\cdot 1a_2+3\cdot 2a_3x+4\cdot 3a_4x^2+\cdots=\sum_{\lambda=0}^{\infty}\lambda(\lambda-1)a_\lambda x^{\lambda-2}$$

$$2\cdot 1a_2+3\cdot 2a_3x+4\cdot 3a_4x^2+\cdots-2x(a_1+2a_2x+3a_3x^2+4a_4x^3+\cdots)$$
$$+2\alpha(a_0+a_1x+a_2x^2+a_3x^3+\cdots)=0$$
$$(2\alpha a_0+2\cdot 1a_2)+(2\alpha a_1-2a_1+3\cdot 2a_3)x+(2\alpha a_2-2\cdot 2a_2+4\cdot 3a_4)x^2$$
$$+\cdots+\{2\alpha a_\lambda-2\lambda a_\lambda+(\lambda+2)(\lambda+1)a_{\lambda+2}\}x^\lambda+\cdots=0$$

恒等式

第$\lambda$-1項 $:2\alpha a_\lambda-2\lambda a_\lambda+(\lambda+2)(\lambda+1)a_{\lambda+2}=0\to a_{\lambda+2}=\frac{2(\lambda-\alpha)}{(\lambda+2)(\lambda+1)}a_\lambda$

解は以下の2つの特殊解の和

① : $y=a_0\left\{1-\frac{2\alpha}{2!}x^2+\frac{2^2\alpha(\alpha-2)}{4!}x^4+\cdots+(-2)^r\frac{\alpha(\alpha-2)\cdots(\alpha-2r+2)}{(2r)!}x^{2r}+\cdots\right\}$

② : $y=a_1x\left\{1-\frac{2(\alpha-1)}{3!}x^2+\frac{2^2(\alpha-1)(\alpha-3)}{5!}x^4+\cdots+(-2)^r\frac{(\alpha-1)(\alpha-3)\cdots(\alpha-2r+1)}{(2r+1)!}x^{2r}+\cdots\right\}$

$$\xi=\sqrt{\beta}x,f(x)=H(\xi)$$

$\frac{\partial^2H}{\partial\xi^2}-2\xi\frac{\partial H}{\partial\xi}+\left(\frac{\varepsilon}{\beta}-1\right)H(\xi)=0\to$ *Hermite*の微分方程式

一般解 : $\phi=f(x)\exp(-\beta x^2/2)=H(\xi)\exp(-\xi^2/2)$

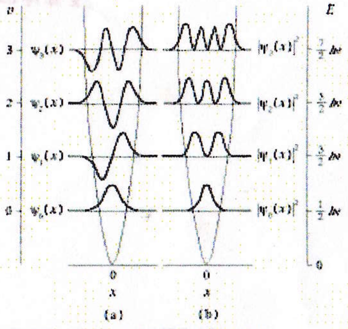
$\to H(\xi)$は有限な多項式（正整数$\alpha$が偶数 : $a_1=0$, $\alpha$が奇数 : $a_0=0$）

$$\alpha=n=\frac{1}{2}\left(\frac{\varepsilon}{\beta}-1\right),\varepsilon=2\left(n+\frac{1}{2}\right)\beta$$

$$E_n=\left(n+\frac{1}{2}\right)\frac{\omega h}{2\pi}=\left(n+\frac{1}{2}\right)h\nu$$

$$\phi_n=\left\{\left(\frac{\beta}{\pi}\right)^{1/2}\frac{1}{n!2^n}\right\}^{1/2}\exp(-\beta x^2/2)H_n(\sqrt{\beta}x)$$

| $n$ | $H_n(\xi)$ |
|---|---|
| 0 | 1 |
| 1 | $2\xi$ |
| 2 | $4\xi^2-2$ |
| 3 | $8\xi^3-12\xi$ |




調和振動子の波動関数