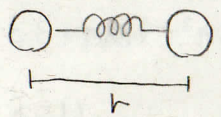
非調和な振動子(摂動法)

☆二原子分子の例



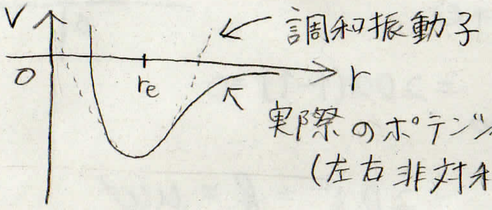
最安定でも振動(零点振動)

$r \to 0$ のとき

立体障害による不安定化

$r \to \infty$ のとき

結合が切れて、振動しない



$x = r - r_e$ とする

r_e: 平衡核間距離

$$V = V_0 + \left(\frac{dV}{dx}\right)_{x=0} x + \frac{1}{2!}\left(\frac{d^2V}{dx^2}\right)_{x=0} x^2 + \cdots$$

4次の項まで考慮

$r \to 0$ のとき $V \sim \frac{1}{2}kx^2$ より

$$V_0 = 0,\ \left(\frac{dV}{dx}\right)_{x=0} = 0$$

$$V = \frac{1}{2}kx^2 + ax^3 + bx^4$$

☆ エルミート多項式が満たす漸化式

・調和振動子の解

$$\psi_n(\xi) = N_n H_n(\xi) \exp\left(-\frac{1}{2}\xi^2\right)$$

$$\xi = \left(\frac{m\omega}{\hbar}\right)^{\frac{1}{2}} x,\ \omega = \left(\frac{k}{m}\right)^{\frac{1}{2}}$$

$$N_n = \left(\frac{1}{2^n n!}\sqrt{\frac{m\omega}{\pi\hbar}}\right)^{\frac{1}{2}},\ E_n = \left(n + \frac{1}{2}\right)\hbar\omega$$

$$H_n = (-1)^n \exp(\xi^2) \frac{d^n}{dx^n} \exp(-\xi^2)$$

・H_n の漸化式

$\exp(-t^2 + 2\xi t) = \sum_{n=0}^{\infty} \frac{H_n(\xi)}{n!} t^n$ という関係より.

$\xi H_n = n H_{n-1} + \frac{1}{2} H_{n+1}$ を満たす.

$$\begin{cases} \xi H_{n-1} = (n-1) H_{n-2} + \frac{1}{2} H_n \\ \xi H_{n+1} = (n+1) H_n + \frac{1}{2} H_{n+2} \end{cases}$$ より

$$\xi H_n = \frac{n}{\xi}\left\{(n-1)H_{n-2} + \frac{1}{2}H_n\right\} + \frac{1}{2\xi}\left\{(n+1)H_n + \frac{1}{2}H_{n+2}\right\}$$

$$\xi^2 H_n = n(n-1)H_{n-2} + \frac{1}{2}(2n+1)H_n + \frac{1}{4}H_{n+2}$$

$$\xi^3 H_n = n(n-1)(n-2)H_{n-3} + \frac{3}{2}n^2 H_{n-1} + \frac{3}{4}(n+1)H_{n+1} + \frac{1}{8}H_{n+3}$$

$$\xi^4 H_n = n(n-1)(n-2)(n-3)H_{n-4} + (2n^3 - 3n^2 + n)H_{n-2} + \frac{1}{4}(6n^2 + 6n + 3)H_n + \frac{1}{4}(2n+3)H_{n+2} + \frac{1}{16}H_{n+4}$$

・エネルギーの補正項

$$E_n^{(1)} = \int_{-\infty}^{\infty} \psi_n^{(0)*} (ax^3 + bx^4) \psi_n^{(0)} dx$$

$$= a\left(\frac{\hbar}{\mu\omega}\right)^{\frac{3}{2}} N_n^2 \int_{-\infty}^{\infty} H_n \xi^3 H_n \exp(-\xi^2) d\xi + b\left(\frac{\hbar}{\mu\omega}\right)^2 N_n^2 \int_{-\infty}^{\infty} H_n \xi^4 H_n \exp(-\xi^2) d\xi$$

μ: 換算質量(2物体の運動を1つの物体として考える)

$$\int_{-\infty}^{\infty} H_n H_m \exp(-\xi^2) = \begin{cases} N_n^{-2} & (n = m) \\ 0 & (n \neq m) \end{cases}$$ を利用

$\xi^3 H_n$ には H_n の項がない → $\int_{-\infty}^{\infty} H_n \xi^3 H_n \exp(-\xi^2) d\xi = 0$

$$E_n^{(1)} = b\left(\frac{\hbar}{\mu\omega}\right)^2 N_n^2 \left\{\frac{1}{4}(6n^2+6n+3)\right\} \int_{-\infty}^{\infty} H_n^2 \exp(-\xi^2) d\xi$$

$$= \frac{3}{2} b\left(\frac{\hbar}{\mu\omega}\right)^2 \left(n^2+n+\frac{1}{2}\right)$$

$$E_n^{(2)} = \sum_{m\neq n} \frac{\left(\int_{-\infty}^{\infty} \psi_m^{(0)*} H' \psi_n^{(0)} dx\right)^2}{E_n^{(0)} - E_m^{(0)}}$$

$$\int_{-\infty}^{\infty} \psi_{n+1}^{(0)*} x^3 \psi_n^{(0)} dx = \left(\frac{\hbar}{\mu\omega}\right)^{\frac{3}{2}} N_{n+1} N_n \frac{3}{4}(n+1) \int_{-\infty}^{\infty} H_{n+1}^2 \exp(-\xi^2) d\xi$$

$$N_n = \left(\frac{1}{2^n n!}\sqrt{\frac{\mu\omega}{\pi\hbar}}\right)^{\frac{1}{2}}$$

$$N_{n+1} = \frac{1}{\sqrt{2(n+1)}} N_n$$

$$\int_{-\infty}^{\infty} \psi_{n+1}^{(0)*} x^3 \psi_n^{(0)} dx = \left(\frac{\hbar}{\mu\omega}\right)^{\frac{3}{2}} \cdot \frac{3}{4}(n+1)\sqrt{2(n+1)}$$

$$= 3\left(\frac{\hbar}{2\mu\omega}\right)^{\frac{3}{2}} (n+1)^{\frac{3}{2}}$$

同様に

$$\int_{-\infty}^{\infty} \psi_{n-1}^{(0)*} x^3 \psi_n^{(0)} dx = 3\left(\frac{\hbar}{2\mu\omega}\right)^{\frac{3}{2}} n^{\frac{3}{2}}$$

$$\int_{-\infty}^{\infty} \psi_{n-3}^{(0)*} x^3 \psi_n^{(0)} dx = \left(\frac{\hbar}{2\mu\omega}\right)^{\frac{3}{2}} \sqrt{n(n-1)(n-2)}$$

$$\int_{-\infty}^{\infty} \psi_{n+3}^{(0)*} x^3 \psi_n^{(0)} dx = \left(\frac{\hbar}{2\mu\omega}\right)^{\frac{3}{2}} \sqrt{(n+3)(n+2)(n+1)}$$

$$E_n^{(0)} - E_m^{(0)} = (n-m)\hbar\omega$$

$$E_n^{(2)} = \left[\left(\frac{\hbar}{2\mu\omega}\right)^3 \frac{n(n-1)(n-2)}{3\hbar\omega} + 9\left(\frac{\hbar}{2\mu\omega}\right)^3 \frac{n^3}{\hbar\omega} - 9\left(\frac{\hbar}{2\mu\omega}\right)^3 \frac{(n+1)^3}{\hbar\omega} - \left(\frac{\hbar}{2\mu\omega}\right)^3 \frac{(n+3)(n+2)(n+1)}{3\hbar\omega}\right] a^2$$

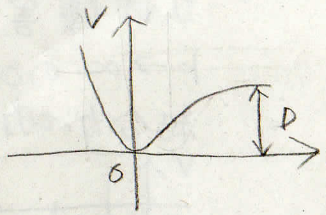
$$E_n^{(2)} = \left[\left(\frac{\hbar}{2\mu\omega}\right)^3 \frac{-9n^2-9n-6}{3\hbar\omega} + 9\left(\frac{\hbar}{2\mu\omega}\right)^3 \frac{-3n^2-3n-1}{\hbar\omega}\right] a^2$$

$$= -\frac{1}{24}\left(\frac{\hbar}{\mu\omega}\right)^3 \cdot \frac{a^2}{\hbar\omega}(90n^2+90n+33)$$

$$= -\frac{15}{4}\left(\frac{\hbar}{\mu\omega}\right)^3 \frac{a^2}{\hbar\omega}\left(n^2+n+\frac{11}{30}\right)$$

例 モースポテンシャル

$$V(x) = D(1-e^{-\alpha x})^2$$



$$V(0) = 0$$

$$\left(\frac{dV}{dx}\right)_{x=0} = 2D\alpha(1-1) = 0$$

$$\left(\frac{d^2V}{dx^2}\right)_{x=0} = 2D\alpha^2 = k = \mu\omega^2$$

$$\alpha = \sqrt{\frac{\mu\omega^2}{2D}}$$

$$\left(\frac{d^3V}{dx^3}\right)_{x=0} = -6D\alpha^3 \qquad a = -D\alpha^3$$

$$\left(\frac{d^4V}{dx^4}\right)_{x=0} = 14D\alpha^4 \qquad b = \frac{7}{12}D\alpha^4$$

$$E_n^{(1)} = \frac{3}{2}\cdot\frac{7}{12}D\alpha^4\left(\frac{\hbar}{\mu\omega}\right)^2\left(n^2+n+\frac{1}{2}\right)$$

$$E_n^{(2)} = -\frac{15}{4}\left(\frac{\hbar}{\mu\omega}\right)^3 \frac{D^2\alpha^6}{\hbar\omega}\left(n^2+n+\frac{11}{30}\right)$$

$\alpha = \sqrt{\frac{\mu\omega^2}{2D}}$ より

$$E_n^{(1)} + E_n^{(2)} = \frac{\hbar^2\omega^2}{32D}\left\{7\left(n^2+n+\frac{1}{2}\right) - 15\left(n^2+n+\frac{11}{30}\right)\right\}$$

$$= -\frac{\hbar^2\omega^2}{4D}\left(n+\frac{1}{2}\right)^2$$