期中考

1.(a) $\lambda_{max} = \rho'(\lambda) = \frac{\rho(\lambda)}{d\lambda} = 0$ 求λ

$\rho(\lambda) = \frac{8\pi hc}{\lambda^5}\left(\frac{1}{e^{hc/\lambda kT}-1}\right)$ ，令 $\frac{hc}{\lambda \cdot k \cdot T} = x$ ，$\lambda = \frac{hc}{x \cdot k \cdot T}$

$$dx = \frac{-hc}{kT} \cdot \frac{1}{\lambda^2} d\lambda = \frac{-hc}{kT}\left(\frac{x \cdot k \cdot T}{h \cdot c}\right)^2 d\lambda = \left(\frac{-kTx^2}{hc}\right) d\lambda$$

$$\frac{d\rho(\lambda)}{d\lambda} = \frac{d\rho(\lambda)}{dx} \cdot \frac{dx}{d\lambda} \text{ (by chain rule)}$$

$$= \left(\frac{-kT}{hc}\right)x^2 \cdot \frac{d\rho(\lambda)}{dx}$$

$$= \left(\frac{-kT}{hc}\right)x^2 \cdot \frac{d}{dx}\left[(8\pi hc)\left(\frac{xkT}{hc}\right)^5 (e^x-1)^{-1}\right] = 0$$

$$= \underbrace{-\left(\frac{kT}{hc}\right)^6 \cdot 8\pi hc}_{\text{常数}} \cdot x^2 \cdot \frac{d}{dx}\left[x^5(e^x-1)^{-1}\right] = 0$$

$$\Rightarrow \frac{d}{dx}\left[x^5(e^x-1)^{-1}\right] \Rightarrow \left[5x^4(e^x-1)^{-1} - x^5 \cdot e^x (e^x-1)^{-2}\right] = 0$$

$$\frac{5x^4}{(e^x-1)} - \frac{x^5e^x}{(e^x-1)^2} = 0$$

$$\frac{5x^4(e^x-1) - x^5e^x}{(e^x-1)^2} = 0 \Rightarrow 5x^4(e^x-1) - x^5e^x = 0 \quad \text{(同除}x^4\text{)}$$

$$\Rightarrow 5e^x - 5 - xe^x = 0 \Rightarrow xe^x = 5e^x - 5$$

利用数值法，求x，$x_{n+1} = x_n - \frac{f(x_n)}{f'(x_n)}$

$x_n = 7 \Rightarrow x_{n+1} = 6.33$

$x_n = 6 \Rightarrow x_{n+1} = 5.49$

$x_n = 5 \Rightarrow x_{n+1} = 4.96$

$x \doteq 4.965$

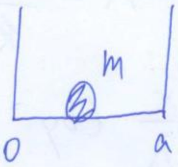
(b) $\lambda_{max} T \cong hc/5k$

$\lambda_{max} = 260\ nm$

$$T = \frac{6.626\times10^{-34}\times2.998\times10^{8}}{5\times1.381\times10^{-23}\times(260\times10^{-9})} = 11064.8\ (K)$$

2、(a) $\hat{H}\psi(x) = E\psi(x)$

$$\frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\psi(x) = E\psi(x)$$



設 $\psi(x) = A\sin kx + B\cos kx$

边界條件

$\psi(0) = 0 \rightarrow B\cos 0 = 0 \Rightarrow B = 0 \rightarrow \psi(x) = A\sin kx$

$\psi(a) = 0 \rightarrow \psi(a) = A\sin ka = 0 \xrightarrow{\sin ka = 0} ka = n\pi \rightarrow k = \frac{n\pi}{a}$

$\rightarrow \psi = A\sin\frac{n\pi x}{a}$, $\int \psi^*(x)\psi(x)\,dx = 1$

$$\Rightarrow A^2\int_0^a \sin^2\frac{n\pi x}{a}\,dx = A^2\int_0^a \frac{1-\cos\frac{2n\pi x}{a}}{2}\,dx = A^2\left[\frac{1}{2}x - \frac{1}{2}\cdot\frac{a}{2n\pi}\underbrace{\sin\left(\frac{2n\pi x}{a}\right)}_{0}\right]\Bigg|_0^a = 1$$

$$= A^2\cdot\frac{1}{2} = 1 \text{ , } A = \sqrt{\frac{2}{a}}$$

$\Rightarrow \psi(x) = \sqrt{\frac{2}{a}}\sin\frac{n\pi}{a}x$

$$\Rightarrow \frac{-\hbar^2}{2m}\frac{\partial^2}{\partial x^2}\left(\sqrt{\frac{2}{a}}\sin\frac{n\pi}{a}x\right) = \frac{-\hbar^2}{2m}\cdot\frac{\partial}{\partial x}\left(\sqrt{\frac{2}{a}}\cdot\frac{n\pi}{a}\cos\frac{n\pi}{a}x\right) = \frac{-\hbar}{2m}\left(\sqrt{\frac{2}{a}}\cdot\left(\frac{n\pi}{a}\right)^2(-\sin\frac{n\pi}{a}x\right)$$

$$\Rightarrow \frac{\hbar^2 n^2\pi^2}{2ma^2}\left(\sqrt{\frac{2}{a}}\sin\frac{n\pi}{a}x\right) = \frac{h^2}{4\pi^2}\frac{n^2\pi^2}{2ma^2}\left(\sqrt{\frac{2}{a}}\sin\frac{n\pi}{a}x\right) = \frac{n^2h^2}{8ma^2}\left(\sqrt{\frac{2}{a}}\sin\frac{n\pi}{a}x\right)$$

$$= E\psi(x)$$

2. (b) trial function $f = x(a-x)$

$$\frac{\int f^* \hat{H} f d\tau}{\int f^* f d\tau} \geq E_0$$

$$\int f^* \hat{H} f d\tau = \int_0^a x(a-x)\left(\frac{-\hbar^2}{2m}\right)\frac{d^2}{dx^2}[x(a-x)]dx$$

$$= \frac{-\hbar^2}{2m}\int_0^a x(a-x)(-2)dx = \frac{-\hbar^2}{2}\left\{\frac{2}{3}x^3 - ax^2\right\}\Big|_0^a = \frac{\hbar^2 a^3}{6m}$$

$$\int f^* f d\tau = \int_0^a x^2(a-x)^2 dx \Rightarrow \left(\frac{1}{3}a^2x^3 - \frac{1}{2}ax^4 + \frac{1}{5}x^5\right)\Big|_0^a = \frac{a^5}{30}$$

$$\Rightarrow \frac{\frac{\hbar^2 a^3}{6m}}{\frac{a^5}{30}} = \frac{5\hbar^2}{ma^2} = \frac{5h^2}{4\pi^2 ma^2} \geq E_0 \left(\frac{h^2}{8ma^2}\right)$$

$$= \frac{5\times(6.626\times10^{-34})^2}{4\pi^2\times m\times a^2} \Rightarrow \frac{5.56\times10^{-68}}{ma^2} \geq \frac{5.48\times10^{-68}}{ma^2}$$

(c) $m = 10^{-27}g = 10^{-30}kg$

$a = 6Å = 6\times10^{-10}m$

$$E = \frac{n^2h^2}{8ma^2} \Rightarrow E_{5\to4} \Rightarrow \Delta E = \frac{5^2h^2}{8ma^2} - \frac{4^2h^2}{8ma^2} = \frac{9h^2}{8ma^2}$$

$$\Delta E = h\nu = h\frac{c}{\lambda}, \quad \frac{9h^{\cancel{2}}}{8ma^2} = \cancel{h}\frac{c}{\lambda} \Rightarrow \lambda = \frac{8ma^2c}{9h}$$

$$\lambda = \frac{8\times10^{-30}\times(6\times10^{-10})^2\times2.998\times10^8}{9\times6.626\times10^{-34}} = 144.79 \text{ (nm)}$$

P3

3. (a) Schrödinger Eq: $\frac{-\hbar}{2m}\cdot\frac{d^2}{dx^2}\psi + \frac{1}{2}kx^2\psi = E\psi$

$$\frac{-\hbar^2}{2m}\frac{d^2}{dx^2}\left[\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}\cdot e^{-\alpha x^2/2}\right] + \frac{1}{2}kx^2\left[\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}\cdot e^{-\alpha x^2/2}\right]$$

$$= \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}\left[\left(\frac{-\hbar^2}{2m}\right)\frac{d}{dx}\left(e^{-\alpha x^2/2}\cdot(-\alpha x)\right) + \frac{1}{2}kx^2 e^{-\alpha x^2/2}\right]$$

$$= \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}\left[\left(\frac{-\hbar^2}{2m}\right)\left(-\alpha\cdot e^{-\alpha x^2/2} + (-\alpha x)^2\cdot e^{-\alpha x^2/2}\right) + \frac{1}{2}kx^2 e^{-\alpha x^2/2}\right]$$

$$= \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}} e^{-\alpha x^2/2}\left[\frac{\alpha\cdot\hbar^2}{2m} - \frac{(\alpha^2 x^2\hbar^2)}{2m} + \frac{1}{2}kx^2\right] \text{ — ①}$$

$\nu = \frac{1}{2\pi}\sqrt{\frac{k}{m}}$, $\alpha = \frac{2\pi\nu m}{\hbar} = \left(\frac{km}{\hbar^2}\right)^{\frac{1}{2}}$ 代入 ①

$$= \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}\cdot e^{-\alpha x^2/2}\left[\left(\frac{km}{\hbar^2}\right)^{\frac{1}{2}}\cdot\frac{\hbar^2}{2m} - \underline{\left(\frac{km}{\hbar^2}\right)\left(\frac{x^2\hbar^2}{2m}\right) + \frac{1}{2}kx^2}\right]$$

$=0$

$$= \left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}\cdot e^{-\alpha x^2/2}\left[\frac{k^{\frac{1}{2}}\cdot m^{\frac{1}{2}}\cdot\hbar}{2m}\right] = \underbrace{\frac{1}{2}\left(\sqrt{\frac{k}{m}}\right)\hbar}_{\text{eigenvalue}}\ \underbrace{\left(\frac{\alpha}{\pi}\right)^{\frac{1}{4}}\cdot e^{-\alpha x^2/2}}_{\text{eigenfunction}}$$

(b)

$H_2 = \nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} \Rightarrow k = 4\pi^2\nu^2\mu = 4\pi^2(c\tilde{\nu})^2\mu$

$$\mu_1 = \frac{m_1 m_2}{m_1+m_2} = \frac{1.0078\times1.0078}{1.0078+1.0078} = 0.5039\ \text{amu} \doteqdot 8.39\times10^{-28}\ \text{kg}$$

$$k = 4\times\pi^2\times(4400\times100\times2.998\times10^8)^2\times8.39\times10^{-28} \doteqdot \underline{576.32\ (N/m)}$$

$$E_0 = \frac{1}{2}h\nu = \frac{1}{2}hc\tilde{\nu} = \frac{1}{2}\times6.626\times10^{-34}\times(4400\times100)\times2.998\times10^8$$

$$\doteqdot 4.37\times10^{-20}\ \text{J} \Rightarrow 4.37\times10^{-20}\times10^{-3}\times6.02\times10^{23}$$

$$= 26.307\ \text{kJ/mol} \doteqdot 26.31\ \text{kJ/mol}$$

$$\doteqdot 6.29\ \text{kcal/mol}$$

3 (c)

彈力常數不影響振動頻率

$$\frac{4400}{\tilde{\nu}_{HD}} = \frac{\sqrt{\frac{1}{\mu_{H_2}}}}{\sqrt{\frac{1}{\mu_{HD}}}} = \frac{\sqrt{\frac{1}{\frac{1.008^2}{1.008\times 2}}}}{\sqrt{\frac{1}{\frac{2.014\times 1.008}{2.014+1.008}}}} = \frac{\sqrt{\frac{2.014\times 1.008}{3.022}}}{\sqrt{\frac{1.008^2}{2.016}}} \Rightarrow 3806.23\,cm^{-1}$$

$$\frac{4400}{\tilde{\nu}_{D_2}} = \frac{\sqrt{\frac{1}{\mu_{H_2}}}}{\sqrt{\frac{1}{\mu_{D_2}}}} = \frac{\sqrt{\frac{1}{\frac{1.008^2}{1.008\times 2}}}}{\sqrt{\frac{1}{\frac{2.014^2}{2.014+2.014}}}} = \frac{\sqrt{\frac{2.014^2}{2.014\times 2}}}{\sqrt{\frac{1.008^2}{1.008\times 2}}} \Rightarrow 3112.84\,cm^{-1}$$

4、

$$E = \frac{l(l+1)\hbar^2}{2I}$$

$$l=0 \Rightarrow 0$$

$$l=1 = \frac{2\hbar^2}{2I} \Rightarrow \Delta E_{0\to 1} = \frac{2\hbar^2}{2I} = \frac{\hbar^2}{\mu r^2} = \frac{h^2}{4\pi^2\mu r^2} = h\nu$$

$$\mu_{AlH} = \frac{1.0078\times 26.9815}{1.0078+26.9815} = 0.9715\,amu = 1.613\times 10^{-27}\,kg$$

$$\nu = c\times\tilde{\nu} = 2.998\times 10^8 \times 12.604\times 100 = 3.7\times 10^{11}$$

$$\Rightarrow r^2 = \frac{h}{4\pi^2\mu\nu} = \frac{6.626\times 10^{-34}}{4\times\pi^2\times 1.61\times 10^{-27}\times 3.7\times 10^{11}}$$

$$r = 1.67\times 10^{-10}\,m = 1.67\,\text{Å}$$

5.(a) Dulong - Petit's law

在高溫下,固体晶格熱是定值等於 25 J/mole

$U = 3N_A\,kT = 3RT$

$C_v = \frac{\partial U}{\partial T} = 3R \sim 25\,J/mol$

N_A:總原子数, k:波兹曼常数

(b) at high temperature

$C_{vm} = 3Rf^2$, $f = \frac{\theta_E}{T}\left(\frac{e^{\theta_E/2T}}{e^{\theta_E/T}-1}\right)$

$T \to \infty$

$\Rightarrow \frac{\theta_E}{T} \to 0$

$\Rightarrow e^{\theta_E/T} \cong 1+\frac{\theta_E}{T}$ $\Rightarrow f = \cancel{\frac{\theta_E}{T}}\left(\frac{1+\frac{\theta_E}{2T}}{\cancel{\frac{\theta_E}{T}}}\right) \simeq 1$

$e^{\theta_E/2T} \cong 1+\frac{\theta_E}{2T}$

$C_{vm} = 3Rf^2 \Rightarrow C_{vm} \simeq 3R$

at low temperature

$T \to 0$

$f = \frac{\theta_E}{T}\left(\frac{e^{\theta_E/2T}}{e^{\theta_E/T}-1}\right)$ 可忽略

$C_{vm} = 3Rf^2 = 0$

$= \frac{\theta_E}{T}\left(e^{-\theta_E/2T}\right) \to 0$

收斂於0 比$\frac{\theta_E}{T}$發散还快

$\frac{\theta_E}{T} \to \infty$

$e^{-\theta_E/2T} \to 0$

(c)

$$C_{vm} = 3Rf^2$$

$$\frac{C_{vm}}{R} = 3f^2 = 3\left[\frac{\theta_E}{T}\left(\frac{e^{\theta_E/2T}}{e^{\theta_E/T}-1}\right)\right]^2 \quad , \theta_E = 300\,K$$

$$T=30 \Rightarrow \frac{C_{vm}}{R} = 3\times\left[\frac{300}{30}\left(\frac{e^{300/60}}{e^{300/30}-1}\right)\right]^2 = 0.01362$$

$$T=60 \Rightarrow \frac{C_{vm}}{R} = 3\times\left[\frac{300}{60}\left(\frac{e^{300/\cancel{60}120}}{e^{300/60}}\right)\right]^2 = 0.5122$$

$$T=120 \Rightarrow \frac{C_{vm}}{R} = 3\times\left[\frac{300}{120}\left(\frac{e^{300/240}}{e^{300/120}-1}\right)\right]^2 = 1.82667$$

$$T=240 \Rightarrow \frac{C_{vm}}{R} = 3\times\left[\frac{300}{240}\left(\frac{e^{300/480}}{e^{300/240}-1}\right)\right]^2 \approx 2.638$$

$$T=600 \Rightarrow \frac{C_{vm}}{R} = 3\times\left[\frac{300}{600}\left(\frac{e^{300/1200}}{e^{300/600}-1}\right)\right]^2 = 2.9$$