期末考解答

1、(a) $\nu_{max} = R'(\nu) = \frac{R(\nu)}{d\nu} = 0$

令 $x = \frac{h\nu}{kT}$, $\nu = \frac{x \cdot k \cdot T}{h}$, $dx = \frac{h}{kT} d\nu$

代回 $R(\nu) d\nu = \frac{2\pi h}{c^2} \cdot \frac{\nu^3}{e^{h\nu/kT} - 1} d\nu$

$$R(\nu) = R(x) = \frac{2\pi h}{c^2} \times \frac{(x \cdot kT/h)^3}{e^x - 1} = \frac{2\pi \cdot k^3 \cdot T^3}{c^2 h^2} \cdot \frac{x^3}{e^x - 1}$$

$$\frac{dR(\nu)}{d\nu} = \frac{dR(x)}{dx} \frac{dx}{d\nu} = \frac{h}{kT} \times \frac{dR(x)}{dx}$$

by chain rule

$$= \frac{h}{kT} \cdot \frac{d}{dx} \left(\frac{2\pi \cdot k^3 T^3}{c^2 h^2} \cdot \frac{x^3}{e^x - 1} \right)$$

$$= \left(\frac{2\pi k^2 T^2}{c^2 h} \right) \frac{d}{dx} \left(\frac{x^3}{e^x - 1} \right) = \frac{2\pi k^2 T^2}{c^2 h} \left[3x^2 (e^x - 1)^{-1} - x^3 (e^x - 1)^{-2} e^x \right]$$

$$= \frac{2\pi \cdot k^2 \cdot T^2}{c^2 \cdot h} \cdot \frac{x^2}{e^x - 1} \left[3 - \frac{x \cdot e^x}{(e^x - 1)} \right] = 0$$

$$3(e^x - 1) - x \cdot e^x = 0$$

$$3e^x - 3 - x \cdot e^x = 0$$ 同除 e^x

$$3 - 3e^{-x} - x = 0 \rightarrow x + 3e^{-x} = 3$$

利用数值分析法求x，公式：$x_{n+1} = x_n - \frac{f(x)}{f'(x)}$

$f(x) = x + 3e^{-x} - 3$, $f'(x) = 1 - 3e^{-x}$

令 $x_0 = 2.8$ (try) , $x_1 = x_0 - \frac{x_0 + 3 \cdot e^{-x_0} - 3}{1 - 3 \cdot e^{-x_0}}$, $x_1 = \underline{2.8214}9029$

$x_2 = \underline{2.8214}37$

$x_3 = \underline{2.821450}$

$x \cong \underline{2.8214}$

(b) $\nu_{max} = \frac{2.8214\,kT}{h}$, $T = \frac{\nu_{max} \cdot h}{2.8214 \cdot k}$

$$T = \frac{3.5 \times 10^{14} \times 6.626 \times 10^{-34}}{2.8214 \times 1.381 \times 10^{-23}} = \underline{5.95 \times 10^{3} (K)}$$

2、(a) $H^{79}Br$ $\bar{\nu} = 2630\,cm^{-1}$. $\nu = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}}$

$$\bar{\nu} = \frac{\nu}{c} = \frac{1}{\lambda} , \nu = c\bar{\nu} = (2.998 \times 10^{8}) m/s \times (2630 \times 10^{2} m^{-1})$$
$$= 7.885 \times 10^{13} s^{-1}$$

$$\mu_{HBr} = \frac{1.0078 \times 78.9183}{1.0078 + 78.9183} (amu) \times 1.66054 \times 10^{-27} kg = 1.652 \times 10^{-27} kg$$

ZPE (in kcal/mol)

$$E_0 = \frac{1}{2} h\nu = \frac{1}{2} \times 6.626 \times 10^{-34} \times 7.885 \times 10^{13} (s^{-1}) = 2.612 \times 10^{-20} J/个 \quad \left(\begin{array}{l}\times 6.02 \times 10^{23} \\ \div 4.184\end{array}\right)$$
$$= 3758.61 \left(\frac{cal}{mol}\right)$$
$$\fallingdotseq \underline{3.76 \left(\frac{kcal}{mol}\right)}$$

(b)

$$\nu = c \cdot \bar{\nu} = \frac{1}{2\pi}\sqrt{\frac{k}{\mu}} , \mu_{DBr} = \frac{2.014 \times 78.9183}{2.014 + 78.9183} \times 1.66054 \times 10^{-27} = 3.261 \times 10^{-27} kg$$

$$\frac{\bar{\nu}_{DBr}}{\bar{\nu}_{HBr}} = \sqrt{\frac{\frac{1}{\mu_{DBr}}}{\frac{1}{\mu_{HBr}}}} = \sqrt{\frac{\mu_{HBr}}{\mu_{DBr}}} \Rightarrow \frac{\bar{\nu}_{DBr}}{2630 cm^{-1}} = \sqrt{\frac{1.652 \times 10^{-27}}{3.261 \times 10^{-27}}} = 0.71$$

$$\bar{\nu}_{DBr} = 0.71 \times 2630 (cm^{-1})$$
$$= \underline{1867.3 (cm^{-1})}$$

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

$$\Delta E_{1\to 0} = \frac{\hbar^2}{2\mu r^2}(2-0) = \frac{\hbar^2}{\mu r^2} = h\nu$$

$$\left(\frac{h}{2\pi}\right)^2 \times \frac{1}{\mu r^2} = h\nu = h \times \bar{\nu} \times c$$

$$r^2 = \frac{h}{4\pi^2} \times \frac{1}{\mu_{HBr} \cdot \bar{\nu} \cdot c} = \frac{6.626\times10^{-34}}{4\pi^2} \times \frac{1}{(1.652\times10^{-27}kg \times 1672 m^{-1} \times 2.998\times10^{8} m/s)}$$

$$r = 1.42 \mathring{A}$$

$$\longrightarrow$$

3. (a)

$$\langle r \rangle = \int_0^\infty\int_0^\pi\int_0^{2\pi} \psi^* r \psi\, r^2 \sin\theta\, dr d\theta d\phi$$

$$= \int_0^\infty\int_0^\pi\int_0^{2\pi} \left(\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}\right) r \left(\frac{1}{\sqrt{\pi}}\left(\frac{1}{a_0}\right)^{3/2} e^{-r/a_0}\right) r^2 \sin\theta\, dr d\theta d\phi$$

$$= \frac{1}{\pi \cdot a_0^3} \int_0^\infty\int_0^\pi\int_0^{2\pi} r^3 \cdot e^{-2r/a_0} \cdot \sin\theta\, dr d\theta d\phi$$

$$= \frac{1}{\pi a_0^3} \int_0^\infty\int_0^\pi r^3 \cdot e^{-2r/a_0} \cdot 2\pi \cdot \sin\theta\, dr d\theta$$

$$= \frac{1}{\pi a_0^3} \int_0^\infty r^3 \cdot e^{-2r/a_0} \cdot 2\pi \cdot 2 \cdot dr = \frac{4}{a_0^3}\int_0^\infty r^3 \cdot e^{-2r/a_0} dr$$

$$= \frac{4}{a_0^3} \frac{3!}{\left(\frac{2}{a_0}\right)^4} \Rightarrow \frac{3a_0}{2} \text{ (average r)}$$

$$\langle r^2 \rangle = \int_0^\infty\int_0^\pi\int_0^{2\pi} \psi^* r^2 \psi\, r^2 \sin\theta\, dr d\theta d\phi$$

$$= \frac{1}{\pi \cdot a_0^3}\int_0^\infty\int_0^\pi\int_0^{2\pi} r^4 \cdot e^{-2r/a_0} \sin\theta\, dr d\theta d\phi$$

$$= \frac{1}{\pi a_0^3}\int_0^\infty\int_0^\pi r^4 \cdot e^{-2r/a_0} \cdot 2\pi \cdot \sin\theta\, dr d\theta = \frac{1}{\pi a_0^3}\int_0^\infty r^4 \cdot e^{-2r/a_0} \cdot 4\pi\, dr$$

$$= \frac{4}{a_0^3}\int_0^\infty r^4 \cdot e^{-2r/a_0} dr$$

$$= \frac{4}{a_0^3} \cdot \frac{4!}{\left(\frac{2}{a_0}\right)^5} = 3a_0^2$$

stand deviation : $\sqrt{\langle r^2\rangle - \langle r\rangle^2}$

$$\Rightarrow \sqrt{3a_0^2 - \left(\frac{3a_0}{2}\right)^2} = \frac{\sqrt{3}}{2} a_0$$

(b)

$$\langle V\rangle = \left\langle \frac{-e^2}{4\pi\varepsilon_0 r} \right\rangle$$

$$= \frac{-e^2}{4\pi\varepsilon_0} \left\langle \frac{1}{r} \right\rangle$$

$$\left\langle \frac{1}{r} \right\rangle = \int_0^\infty \int_0^\pi \int_0^{2\pi} \psi^* \frac{1}{r} \psi \, r^2 \sin\theta \, dr \, d\theta \, d\phi$$

$$= \frac{1}{\pi a_0^3} \int_0^\infty \int_0^\pi \int_0^{2\pi} r \cdot e^{-2r/a_0} \sin\theta \, dr \, d\theta \, d\phi$$

$$= \frac{1}{\pi a_0^3} \int_0^\infty \int_0^\pi r \cdot e^{-2r/a_0} \cdot 2\pi \sin\theta \, dr \, d\theta$$

$$= \frac{1}{\pi \cdot a_0^3} \int_0^\infty r \cdot e^{-2r/a_0} \cdot 2\pi \cdot 2 \, dr = \frac{4}{a_0^3} \int_0^\infty r \cdot e^{-2r/a_0} \, dr$$

$$= \frac{4}{a_0^3} \frac{1}{\left(\frac{2}{a_0}\right)^2} = \frac{1}{a_0}$$

$$\langle V\rangle = \frac{-e^2}{4\pi\varepsilon_0 a_0}$$

(c) $n=3 \longrightarrow n=2$

$$\Delta E = \frac{-Z^2 e^2}{8\pi\varepsilon_0 a} \left(\frac{1}{3^2} - \frac{1}{2^2}\right) = 1.89\,\text{eV} \doteqdot 3.03 \times 10^{-19}\,\text{J}$$

$$\Delta E = h\nu = h\frac{c}{\lambda} \Rightarrow \lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-34} \times 2.998 \times 10^{8}}{3.03 \times 10^{-19}}$$

$$\doteqdot 6.55 \times 10^{-7}\,(\text{m}) \doteqdot 655\,(\text{nm})$$

4(a) ~~Hartre~~ Hartree-Fock method：最基本的一种量化計算理論，以行列式来近似分子的波函数。此种行列式也被稱作 slater determinants

$$\psi_{HF}=\frac{1}{\sqrt{(2n)!}}\begin{vmatrix} \phi_1\alpha(1) & \phi_1\beta(1) & \phi_2\alpha(1) & \phi_2\beta(1) & \cdots & \phi_n\alpha(1) & \phi_n\beta(1) \\ \phi_1\alpha(2) & \phi_1\beta(2) & \phi_2\alpha(2) & \phi_2\beta(2) & \cdots & \phi_n\alpha(2) & \phi_n\beta(2) \\ \vdots & \vdots & \vdots & & & & \\ \phi_1\alpha(2n) & \phi_1\beta(2n) & \phi_2\alpha(2n) & \phi_2\beta(2n) & \cdots & \phi_n\alpha(2n) & \phi_n\beta(2n) \end{vmatrix}$$

(b) 傳统上 STO 对多原子分子的計算是很没效率的， $f_{GTO}=Nx^iy^jz^ke^{-\zeta r^2}$

我們以 Gaussian-type funtion (GTO)，以 GTO 的線性组合来逼近類似 STO 的 contracted Gaussian-type funtion (CGTF) 因 GTO 降低計算双电子積分的時間，效率提高。

(c) 6-31+G(d,p)，HCHO

H：
1s：1×2
1p：3
5

C,O：
1s：1
2s 2p：4×2+4
1d：5
18

5×2+18×2
= 46 个 basis function

(d) H C H O
↓ ↓ ↓ ↓ e数
1 6 1 8

總e^-数：1+6+1+8=16 (8 个 occupied)

46-8=38 (unoccupied)

5 (a)

m_{l_1}	m_{l_2}	m_{s1}	m_{s2}	M_L	M_S
-1	-1	$\frac{1}{2}$	$-\frac{1}{2}$	-2	0
-1	0	$\frac{1}{2}$	$-\frac{1}{2}$	-1	0
-1	0	$\frac{1}{2}$	$\frac{1}{2}$	-1	1
-1	0	$\frac{-1}{2}$	$\frac{1}{2}$	-1	0
-1	0	$\frac{-1}{2}$	$\frac{-1}{2}$	-1	-1
-1	1	$\frac{1}{2}$	$\frac{-1}{2}$	0	0
-1	1	$\frac{1}{2}$	$\frac{1}{2}$	0	1
-1	1	$\frac{-1}{2}$	$\frac{1}{2}$	0	0
-1	1	$\frac{-1}{2}$	$\frac{-1}{2}$	0	-1
0	0	$\frac{1}{2}$	$\frac{-1}{2}$	0	0
1	0	$\frac{1}{2}$	$\frac{-1}{2}$	1	0
1	0	$\frac{1}{2}$	$\frac{1}{2}$	1	1
1	0	$\frac{-1}{2}$	$\frac{1}{2}$	1	0
1	0	$\frac{-1}{2}$	$\frac{-1}{2}$	1	-1
1	1	$\frac{1}{2}$	$\frac{-1}{2}$	2	0

M_L \ M_S	-1	0	1
2		1	
1	1	2	1
0	1	3	1
-1	1	2	1
-2		1	

M_L \ M_S	0
0	1

$\rightarrow {}^1S_0$

M_L \ M_S	-1	0	1
1	1	1	1
0	1	1	1
-1	1	1	1

↓

${}^3P_0\ {}^3P_1\ {}^3P_2$

M_L \ M_S	0
2	1
1	1
0	1
-1	1
-2	1

$\rightarrow {}^1D_2$

(b) $L = \overset{\overset{s}{\uparrow}}{0},\overset{\overset{p}{\uparrow}}{1},\overset{\overset{d}{\uparrow}}{2},3$ ——— $|L-S| \le J \le |L+S|$

	S	L	J	term symbol
H: $\frac{\uparrow}{1s}$	$\frac{1}{2}$	0	$\frac{1}{2}$	$^2S_{\frac{1}{2}}$
He: $\frac{\uparrow\downarrow}{1s}$	0	0	0	$^1S_0$
Li: $\frac{\uparrow}{2s}$	$\frac{1}{2}$	0	$\frac{1}{2}$	$^2S_{\frac{1}{2}}$
Be: $\frac{\uparrow\downarrow}{2s}$	0	0	0	$^1S_0$
B: $\underset{2p}{}\ \underset{1}{\underline{\uparrow}}\ \underset{0}{\underline{\quad}}\ \underset{-1}{\underline{\quad}}$	$\frac{1}{2}$	1	$\frac{1}{2},\frac{3}{2}$	$^2P_{\frac{1}{2}}$ [軌域电子未超过半填满取J值小的]
C: $\underset{1}{\underline{\uparrow}}\ \underset{0}{\underline{\uparrow}}\ \underset{-1}{\underline{\quad}}$	1	1	0.1,2	$^3P_0$
N: $\underset{1}{\underline{\uparrow}}\ \underset{0}{\underline{\uparrow}}\ \underset{-1}{\underline{\uparrow}}$	$\frac{3}{2}$	0	$\frac{3}{2}$	$^4S_{\frac{3}{2}}$
O $\underline{\uparrow\downarrow}\ \underline{\uparrow}\ \underline{\uparrow}$	1	1	0,1,2	$^3P_2$ [軌域电子超过半填满取J值最大]
F $\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow}$	$\frac{1}{2}$	1	$\frac{1}{2},\frac{3}{2}$	$^2P_{\frac{3}{2}}$
Ne $\underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}\ \underline{\uparrow\downarrow}$	0	0	0	$^1S_0$

6、(a)

① $H_2: (\sigma_{g1s})^2$

② $C_2: (\sigma_{g,1s})^2 (\sigma^*_{u,1s})^2 (\sigma_{g,2s})^2 (\sigma^*_{u,2s})^2 (\pi_{u,2p})^4$

③ $CN^-: (\sigma_{g,1s})^2 (\sigma^*_{u,1s})^2 (\sigma_{g,2s})^2 (\sigma^*_{u,2s})^2 (\pi_{u,2p})^4 (\sigma_{g,2p})^2$

④ $O_2: (\sigma_{g1s})^2 (\sigma^*_{u,1s})^2 (\sigma_{g,2s})^2 (\sigma^*_{u2s})^2 (\sigma_{g,2p})^2 (\pi_{u,2p})^4 (\pi^*_{g,2p})^2$

⑤ $NO: (\sigma_{g1s})^2 (\sigma^*_{u1s})^2 (\sigma_{g2s})^2 (\sigma^*_{u2s})^2 (\sigma_{g2p})^2 (\pi_{u,2p})^4 (\pi^*_{g2p})^1$

(b)

(1) bond order

① $H_2: \frac{2-0}{2} = 1$

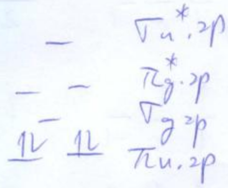
② $C_2: \frac{4-0}{2} = 2$

③ $CN^-: \frac{6-0}{2} = 3$

④ $O_2: \frac{6-2}{2} = 2$

⑤ $NO: \frac{6-1}{2} = 2.5$

$B_2 \sim N_2$



(2)

① $H_2: {}^1\Sigma$

② $C_2: {}^1\Sigma$

③ $CN^-: {}^1\Sigma$

④ $O_2: {}^3\Sigma$

⑤ $NO: {}^2\Pi$

7.  by ~~Huk~~ Huckel theory, $\alpha > 0$, $\beta < 0$

$$\begin{vmatrix} \alpha - E_\pi & \beta & 0 & \beta \\ \beta & \alpha - E_\pi & \beta & 0 \\ 0 & \beta & \alpha - E_\pi & \beta \\ \beta & 0 & \beta & \alpha - E_\pi \end{vmatrix} = 0 \xrightarrow{\text{簡化}} \begin{vmatrix} \frac{\alpha - E_\pi}{\beta} & 1 & 0 & 1 \\ 1 & \frac{\alpha - E_\pi}{\beta} & 1 & 0 \\ 0 & 1 & \frac{\alpha - E_\pi}{\beta} & 1 \\ 1 & 0 & 1 & \frac{\alpha - E_\pi}{\beta} \end{vmatrix}$$

令 $\frac{\alpha - E_\pi}{\beta} = x$

$$\Rightarrow \begin{vmatrix} x & 1 & 0 & 1 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 1 & 0 & 1 & x \end{vmatrix} = 0 \xrightarrow{\text{降階}} x \begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} - \begin{vmatrix} 1 & 1 & 0 \\ 0 & x & 1 \\ 1 & 1 & x \end{vmatrix} - \begin{vmatrix} 1 & x & 1 \\ 0 & 1 & x \\ 1 & 0 & 1 \end{vmatrix} = 0$$

$\Rightarrow x^4 - 4x^2 = 0$

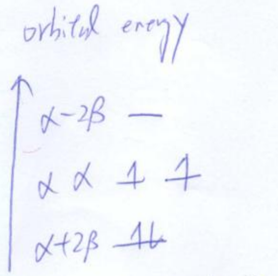
$x^2(x^2-4) = 0$

$x = \underset{\text{重根}}{\underline{0, 0}}, 2, 2$

$\frac{\alpha - E_\pi}{\beta} = 0$, $E_\pi = \alpha, \alpha$

$\frac{\alpha - E_\pi}{\beta} = 2$, $E_\pi = \alpha - 2\beta$

$\frac{\alpha - E_\pi}{\beta} = -2$, $E_\pi = \alpha + 2\beta$



E_π (cyclobutandiene)
$= 4\alpha + 4\beta$

E_π (ethylene) $= 2\alpha + 2\beta$

delocalization Energy $\Rightarrow (4\alpha + 4\beta) - 2(2\alpha + 2\beta) = 0$