第一章

8. $\nu_1 = \dfrac{c}{\lambda_1} = \dfrac{3 \times 10^8}{589.593 \times 10^{-9}} = 5.088 \times 10^{14}(s^{-1})$

$\nu_2 = \dfrac{c}{\lambda_2} = \dfrac{3 \times 10^8}{588.996 \times 10^{-9}} = 5.093 \times 10^{14}(s^{-1})$

$\widetilde{\nu}_1 = \dfrac{1}{\lambda_1} = \dfrac{1}{589.593 \times 10^{-9}} = 1.696 \times 10^6(m^{-1})$

$\widetilde{\nu}_2 = \dfrac{1}{\lambda_2} = \dfrac{1}{588.996 \times 10^{-9}} = 1.698 \times 10^6(m^{-1})$

$E_1 = h\nu_1 = 6.626 \times 10^{-34} \times 5.088 \times 10^{14} \times 6.02 \times 10^{23} \times 10^{-3} = 203.075(kJ \cdot mol^{-1})$

$E_2 = h\nu_2 = 6.626 \times 10^{-34} \times 5.093 \times 10^{14} \times 6.02 \times 10^{23} \times 10^{-3} = 203.275(kJ \cdot mol^{-1})$

9. $\dfrac{1}{2}m\upsilon^2 = hc(\dfrac{c}{\lambda} - \nu_0)$

$\upsilon_m = \sqrt{\dfrac{2h(\dfrac{c}{\lambda} - \nu_0)}{m}} = \sqrt{\dfrac{2 \times 6.626 \times 10^{-34}(\dfrac{3 \times 10^8}{300 \times 10^{-9}} - 5.464 \times 10^{14})}{9.1 \times 10^{-31}}} = 8.130 \times 10^5(m \cdot s^{-1})$

$p = m\upsilon_m = 9.1 \times 10^{-31} \times 8.130 \times 10^5 = 7.398 \times 10^{-25}(kg \cdot m \cdot s^{-1})$

$\lambda = \dfrac{h}{p} = \dfrac{6.626 \times 10^{-34}}{7.398 \times 10^{-25}} = 8.96 \times 10^{-10}(m)$

10. (1) $\lambda = \dfrac{h}{p} = \dfrac{h}{m\upsilon} = \dfrac{6.626 \times 10^{-34}}{10^{-10} \times 0.01} = 6.626 \times 10^{-22}(m)$

(2) $\lambda = \dfrac{h}{p} = \dfrac{h}{\sqrt{2mT}} = \dfrac{6.626 \times 10^{-34}}{\sqrt{2 \times 1.67 \times 10^{-37} \times 100 \times 1.6 \times 10^{-19}}} = 2.87 \times 10^{-12}(m)$

(3)

$\lambda = \dfrac{h}{p} = \dfrac{h}{\sqrt{2mT}} = \dfrac{h}{\sqrt{2meV}} = \dfrac{6.626 \times 10^{-34}}{\sqrt{2 \times 9.1 \times 10^{-31} \times 2 \times 10^5 \times 1.6 \times 10^{-19}}} = 2.75 \times 10^{-12}(m)$

11. 子弹：$\Delta x \geq \dfrac{h}{m \cdot \Delta \upsilon} = \dfrac{6.626 \times 10^{-34}}{0.01 \times 1000 \times 10\%} \geq 6.63 \times 10^{-34}(m)$ 可忽略

花粉：$\Delta x \geq \dfrac{h}{m \cdot \Delta \upsilon} = \dfrac{6.626 \times 10^{-34}}{10^{-13} \times 1 \times 10\%} \geq 6.63 \times 10^{-20}(m)$ 可忽略

电子：$\Delta x \geq \dfrac{h}{m \cdot \Delta \upsilon} = \dfrac{6.626 \times 10^{-34}}{9.1 \times 10^{-31} \times 10^6 \times 10\%} \geq 7.27 \times 10^{-9}(m)$　不能忽略

只有不确定关系具有实际意义

12. 证明：$\Delta x = \lambda$ 因为 $\Delta x \Delta p_x \geq h \Rightarrow \Delta x \cdot m \Delta \upsilon \geq h$

$$\Delta \upsilon \geq \frac{h}{m \cdot \Delta x} = \frac{h}{m \cdot \lambda} = \frac{p}{m} = \upsilon$$

13. $eV = \dfrac{1}{2} m \upsilon^2 \Rightarrow \upsilon = \sqrt{\dfrac{2eV}{m}}$　　$\Delta \upsilon = 0.1 \upsilon$

$$\Delta x \geq \frac{h}{m \cdot \Delta \upsilon} = \frac{h}{0.1\sqrt{2m_e V}} = \frac{6.626 \times 10^{-34}}{0.1 \times \sqrt{2 \times 0.91095 \times 10^{-30} 1.60219 \times 10^{-19} \times 1000}}$$

$= 3.88 \times 10^{-10}(m)$　对成像没有影响

若用　$\Delta x \Delta p_x \geq \dfrac{h}{4\pi}$

$\Delta x \geq 3.09 \times 10^{-11}(m)$

14. （1）$\dfrac{d^2}{dx^2}(e^{imx}) = -m^2 \cdot e^{imx}$　是　本征值：$-m^2$

（2）$\dfrac{d^2}{dx^2}(\sin x) = -\sin x$　是　本征值：-1

（3）$\dfrac{d^2}{dx^2}(x^2 + y^2) = 2$　不是

（4）$\dfrac{d^2}{dx^2}[(a-x)e^{-x}] = e^{-x}(2 + a - x)$　不是

16. $i\dfrac{d}{d\phi} e^{im\phi} = ie^{im\phi} \cdot im = -me^{im\phi}$　是。本征值是-m

$i\dfrac{d}{d\phi} \sin m\phi = i\cos m\phi \cdot m = im\cos m\phi$　不是

17. （1）$\Delta E_n = E_{n+1} - E_n = \dfrac{(2n+1)h^2}{8ml^2}$

$\therefore \Delta E_1 = \dfrac{3h^2}{8ml^2} = \dfrac{3 \times (6.626 \times 10^{-34})^2}{8 \times 0.91095 \times 10^{-20} \times (200 \times 10^{-12})^2} = 4.52 \times 10^{-18} J$

$$\lambda = \frac{hc}{\Delta E} = \frac{6.626 \times 10^{-34} \times 3 \times 10^8}{4.52 \times 10^{-18}} = 4.40 \times 10^{-8} (m)$$

$$\tilde{\nu} = \frac{1}{\lambda} = \frac{1}{4.40 \times 10^{-8}} = 2.27 \times 10^7 (m^{-1})$$

（2）$\langle x^2 \rangle = \int \psi^* \hat{x}^2 \psi dx = \frac{2}{l} \int_0^l x^2 \sin^2 \frac{n_x \pi x}{l} dx = \frac{1}{l} \int_0^l x^2 (1 - \cos \frac{2n_x \pi x}{l}) dx$

$$= \frac{1}{l} \int_0^l x^2 dx - \int_0^l x^2 \cos \frac{2n_x \pi x}{l} dx = \frac{1}{l}(\frac{l^3}{3} - \frac{l^3}{2n_x^2 \pi^2}) = \frac{l^2}{3}(1 - \frac{3}{2n_x^2 \pi^2})$$

$$\approx \frac{l^2}{3}$$

$$\langle x \rangle = \int \psi^* \hat{x} \psi dx = \int_0^l x |\psi(x)|^2 dx = \frac{2}{l} \int_0^l x (\sin \frac{n\pi x}{l})^2 dx = \frac{1}{l} \int_0^l x(1 - \cos \frac{2n\pi x}{l}) dx$$

$$= \frac{1}{l}[\int_0^l x dx - \int_0^l \cos \frac{2n\pi x}{l} dx]$$

$$= \frac{1}{l}(\frac{l}{2})^2 - \frac{1}{l}[\frac{l^2}{4\pi^2 n^2} \cos \frac{2n\pi x}{l}\Big|_0^l + \frac{l}{2\pi n} x \sin \frac{2n\pi x}{l}\Big|_0^l]$$

$$= \frac{1}{l}[\frac{l^2}{2} - 0] = \frac{l}{2}$$

$$\langle p_x \rangle = \int_0^l \psi (-i\hbar \frac{d}{dx}) \psi dx = \frac{2}{l} \cdot \frac{\hbar}{i} \int_0^l \sin \frac{n_x \pi x}{l} \frac{d}{dx} \sin \frac{n_x \pi x}{l} dx$$

$$= \frac{2\hbar}{il} \cdot \frac{n_x \pi}{l} \int_0^l \sin \frac{n_x \pi x}{l} \cos \frac{n_x \pi x}{l} dx$$

$$= \frac{\hbar n_x \pi}{il^2} [\sin^2 \frac{n_x \pi x}{l}\Big|_0^l \cdot \frac{l}{n_x \pi}] = 0$$

$$\hat{p}_x^2 \psi_n(x) = -\hbar^2 \frac{d^2}{dx^2}(\sqrt{\frac{2}{l}} \sin \frac{n\pi x}{l}) = \frac{n^2 h^2}{4l^2} \psi_n(x)$$

$$\therefore \overline{p}^2 = p^2 = \frac{n^2 h^2}{4l^2}$$

18.(1)

$$\int \psi * \psi d\tau = \frac{8}{abc}\int_0^a \sin^2\frac{n_x\pi x}{a}dx\int_0^b \sin^2\frac{n_x\pi y}{b}dy\int_0^c \sin^2\frac{n_x\pi z}{a}dz$$

$$= \frac{8}{abc}[\frac{1}{2}x - \frac{a}{n_x\pi}\cdot\frac{1}{4}\sin\frac{2n_x\pi x}{a}]\Big|_0^a \cdot [\frac{1}{2}y - \frac{b}{n_x\pi}\cdot\frac{1}{4}\sin\frac{2n_x\pi y}{b}]\Big|_0^b \cdot [\frac{1}{2}z - \frac{c}{n_x\pi}\cdot\frac{1}{4}\sin\frac{2n_x\pi z}{c}]\Big|_0^c$$

$$= \frac{8}{abc}\cdot\frac{a}{2}\cdot\frac{b}{2}\cdot\frac{c}{2} = 1$$

(2) n_x, n_y, n_z 为 2，1，1 时

概　　　　　　　　　　　　　　　　　　　　　　　率

$$p_1 = \frac{8}{abc}\int\sin^2\left(\frac{2\pi x}{a}\right)dx\cdot\sin^2\left(\frac{\pi y}{b}\right)dy\cdot\sin^2\left(\frac{\pi z}{a}\right)dz$$

$$= \frac{8}{100^3}\int_{19.95}^{20.05}\sin^2\left(\frac{2\pi x}{100}\right)dx\int_{29.95}^{30.05}\sin^2\left(\frac{\pi y}{100}\right)dy\int_{49.95}^{50.05}\sin^2\left(\frac{\pi z}{100}\right)dz$$

$$= \frac{8}{10^6}\left[\frac{x}{2} - \frac{1}{2}\cdot\frac{100}{4\pi}\sin\left(\frac{4\pi x}{100}\right)\right]\Big|_{19.95}^{20.05}\cdot\left[\frac{y}{2} - \frac{1}{2}\cdot\frac{100}{2\pi}\sin\left(\frac{2\pi x}{100}\right)\right]\Big|_{29.95}^{30.05}\cdot\left[\frac{z}{2} - \frac{1}{2}\cdot\frac{100}{2\pi}\sin\left(\frac{2\pi z}{100}\right)\right]\Big|_{49.95}^{50.05}$$

$$= \frac{8}{10^6}(0.05 + 0.0406)\cdot(0.05 + 0.0151)\cdot(0.05 + 0.05) = 4.7\times10^{-9}$$

同理求得 $p_2 = 6\times10^{-15}$

（3） $E_{n_x,n_y,n_z} = \frac{h^2}{8ma^2}(n_x^2 + n_y^2 + n_z^2)$

	n_x	n_y	n_z		简并度
①	1	1	1	$E_{111} = \frac{3h^2}{8ma^2}$	1
②	2	1	1		
	1	2	1	$E_{211} = \frac{6h^2}{8ma^2}$	3
	1	1	2		
③	2	2	1		
	1	2	2	$E_{221} = \frac{9h^2}{8ma^2}$	3
	2	1	2		

④

$$\begin{cases} 3 \quad 1 \quad 1 \\ 1 \quad 3 \quad 1 \qquad E_{113} = \dfrac{11h^2}{8ma^2} \qquad\qquad 3 \\ 1 \quad 1 \quad 3 \end{cases}$$

⑤ $\quad$ 2 $\quad$ 2 $\quad$ 2 $\qquad E_{222} = \dfrac{12h^2}{8ma^2} \qquad\qquad$ 1

第二章

7. （1） n=3, l=1, m=0, ψ_{310}, 3pz

（2） $E_n = -13.6\dfrac{z^2}{n^2}(ev)$ $\quad E_3 = -13.6\dfrac{z^2}{9}(ev)$

$\quad \langle V \rangle = 2E_3 = -27.2 \times \dfrac{z^2}{9} \quad \langle T \rangle = |E_3| = 13.6 \cdot \dfrac{z^2}{9}$

（3） $|M| = \sqrt{l(l+1)}\hbar = \sqrt{1 \times 2}\hbar = \sqrt{2}\hbar$

$\quad |\mu| = \sqrt{l(l+1)}\mu_B = \sqrt{2}\mu_B$

（4） $\langle r \rangle = \int_0^{2\pi} \psi^* r \psi d\tau = \int_0^{\infty}\int_0^{\pi}\int_0^{2\pi} r\psi^2 r^2 \sin\theta dr d\theta d\varphi$

或 $\langle r \rangle = \dfrac{n^2 a_0}{2}\left\{ 1 + \dfrac{1}{2}\left[1 - \dfrac{l(l+1)}{n^2} \right] \right\} = \dfrac{\pi}{2z}a_0$

（7）令 R. Y=0，则 $\cos\theta = 0 \Rightarrow \theta = 90°$

$\left(6 \cdot \dfrac{zr}{a_0} - \dfrac{z^2 r^2}{a_0^2} \right)e^{-\frac{zr}{3a_0}} = 0 \Rightarrow r = 0, \dfrac{6a_0}{z}, \infty$

$0, \infty$ 不算节面，所以节面有两个，$\theta = 90°$ 为 xy 平面，$r = \dfrac{6a_0}{z}$ 为一球面，半径为 $\dfrac{a_0}{z}$

（9）$\cos\theta = \dfrac{m\hbar}{\sqrt{l(l+1)}\hbar} = 0 \Rightarrow \theta = 90°$

10.（1）Li^{2+} : $\left[-\dfrac{h^2}{8\pi^2 \mu}\nabla^2 - \dfrac{3e^2}{4\pi\varepsilon_0 r} \right]\psi = E\psi$

定核近似

μ： Li^{2+} 约化质量，r:电子到核距离，∇^2：Laplace 算符，ψ：电子状态波函数

h：planck 常数，$\varepsilon_。$：真空电容率，[]内为能量算符，其中第一项是动能算符，第二项是势能算符。

$$Li: \left[-\sum_{j=1}^{3} \frac{h^2}{8\pi^2 \mu} \nabla_j^2 - \sum_{j=1}^{3} \frac{3e^2}{4\pi\varepsilon_0 r_j} + \frac{1}{2}\sum_{j=1}^{3}\sum_{j=1}^{3} \frac{e^2}{4\pi\varepsilon_0 r_{ij}} \right] \psi = E\psi \text{ 或}$$

电子动能项　核与电子吸引势能　电子电子排斥势能

$$\left[-\frac{1}{2}\sum_{j=1}^{3} \nabla_j^2 - \sum_{j=1}^{3} \frac{3}{r_j} + \frac{1}{2}\sum_{j=1}^{3}\sum_{j=1}^{3} \frac{1}{r_{ij}} \right] \psi = E\psi$$

（2）Li^{2+}，单电子原子，E 仅与 n 有关，$E_{3s} = E_{3p} = E_{3d}$

（3）Li，多电子原子，E 与 n.l 有关，$E_{3s} < E_{3p} < E_{3d}$

11.(1)氢原子能量 $E_n = -2.18 \times 10^{-18} \frac{1}{n^2} J$

第一激发态（n=2）和基态（n=1）之间的能量差：

$$\Delta E_1 = E_2 - E_1 = -2.18 \times 10^{-18} \left(\frac{1}{2^2} - \frac{1}{1^2} \right) = 1.64 \times 10^{-18} J$$

$$\Delta E_1 = h\nu_1 \quad \lambda_1 = \frac{ch}{\Delta E_1} = \frac{3.0 \times 10^8 \times 6.626 \times 10^{-34}}{1.64 \times 10^{-18}} = 1.21 \times 10^{-7} (m)$$

第六激发态（n=7）和基态之间的能量差为：

$$\Delta E_6 = E_7 - E_1 = -2.18 \times 10^{-18} \left(\frac{1}{7^2} - \frac{1}{1^2} \right) = 2.14 \times 10^{-18} J$$

$$\lambda_6 = \frac{ch}{\Delta E_6} = \frac{3.0 \times 10^8 \times 6.626 \times 10^{-34}}{2.14 \times 10^{-18}} = 9.29 \times 10^{-8} (m)$$

（2）使处于基态氢原子电离所需最小能量为：

$$\Delta E_\infty = E_\infty - E_1 = -E_1 = 2.18 \times 10^{-18} J$$

而 $\Delta E_1 < \Delta E_\infty \quad \Delta E_6 < \Delta E_\infty$

所以两条谱线所产生的光子均不能使处于基态氢原子电子电离，

而 $\Delta E_1 > W_{Cu} \quad \Delta E_6 > W_{Cu}$

所以两条谱线产生的光子能使铜晶体电离

$$T = \Delta E_n - W_{Cu} \quad \lambda = \frac{h}{p} = \frac{h}{\sqrt{2m\Delta E}}$$

$$\lambda_1 = \frac{6.626 \times 10^{-34}}{\sqrt{2 \times 9.1095 \times 10^{-31} \times (1.64 \times 10^{-18} - 7.44 \times 10^{-19})}} = 5.19 \times 10^{-10} (m)$$

$$\lambda_6 = \frac{6.626 \times 10^{-34}}{\sqrt{2 \times 9.1095 \times 10^{-31} \times (2.14 \times 10^{-18} - 7.44 \times 10^{-19})}} = 4.15 \times 10^{-10} (m)$$
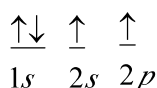
12. Na^+：$\left[-\frac{1}{2} \sum_{i=1}^{10} \nabla_i^2 - \sum_{i=1}^{10} \frac{11}{r_i} + \frac{1}{2} \sum_{i=1}^{10} \sum_{j=1}^{10} \frac{1}{r_{ij}} \right] \psi = E\psi$

F^-：$\left[-\frac{1}{2} \sum_{i=1}^{10} \nabla_i^2 - \sum_{i=1}^{10} \frac{9}{r_i} + \frac{1}{2} \sum_{i=1}^{10} \sum_{j=1}^{10} \frac{1}{r_{ij}} \right] \psi = E\psi$

Hartree 自洽场单电子薛定谔方程：Na^+：$\left(-\frac{1}{2} \nabla_i^2 - \frac{11}{r_i} + \sum_{j \neq i} \int \frac{1}{r_{ij}} |\psi_j|^2 d\tau_j \right) \psi_i = E_i \psi_i$
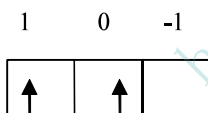
F^-：$\left(-\frac{1}{2} \nabla_i^2 - \frac{9}{r_i} + \sum_{j \neq i} \int \frac{1}{r_{ij}} |\psi_j|^2 d\tau_j \right) \psi_i = E_i \psi_i$

13. Be：$1s^2 2s^1 2p^1$ 共 12 种

$$\underset{1s}{\uparrow\downarrow} \quad \underset{2s}{\uparrow} \quad \underset{2p}{\uparrow}$$

$$\psi(1,2,3,4) = \frac{1}{\sqrt{4!}} \begin{vmatrix} \psi_{1s}(1)\alpha(1) & \psi_{1s}(2)\alpha(2) & \psi_{1s}(3)\alpha(3) & \psi_{1s}(4)\alpha(4) \\ \psi_{1s}(1)\beta(1) & \psi_{1s}(2)\beta(2) & \psi_{1s}(3)\beta(3) & \psi_{1s}(4)\beta(4) \\ \psi_{2s}(1)\alpha(1) & \psi_{2s}(2)\alpha(2) & \psi_{2s}(3)\alpha(3) & \psi_{2s}(4)\alpha(4) \\ \psi_{2p}(1)\alpha(1) & \psi_{2p}(2)\alpha(2) & \psi_{2p}(3)\alpha(3) & \psi_{2p}(4)\alpha(4) \end{vmatrix}$$

14. C：基谱项 $1s^2 2s^2 2p^2$

1	0	-1
↑	↑	

$$L = |M_L|_{max} = \left| \sum M_l \right| = 1 \quad S = |M_s|_{max} = \left| \sum m_{si} \right| = \left| \frac{1}{2} + \frac{1}{2} \right| = 1$$

$J = 2,1,0$ 所以能量最低的谱项（基谱项）：^3P 基谱支项 $^3P_0$

激发态 $p^1 d^1$ $l_1 = 1$ $l_2 = 2$ $L = 3,2,1$

$$s_1 = s_2 = \frac{1}{2} \quad S = 1,0$$

L	3	2	1	所有可能谱项： $^3F, ^3D, ^3P$
1	^3F	^3D	^3P	$^1F, ^1D, ^1P$
0	^1F	^1D	^1P	

15. $C_r: 3d^5 4s^1$ $S = |M_s|_{max} = |\sum m_{si}| = 6 \times \frac{1}{2} = 3$

0 2 1 0 -1 -2 $L = |M_{li}|_{max} = |\sum m_i| = 0$ J=0 $^7S_3$

$C_u: 3d^{10} 4s^1$ $S = \frac{1}{2} \times 6 + (-\frac{1}{2}) \times 5 = \frac{1}{2}$

          $L = 0$ $J = \frac{1}{2}$ $^2S_{\frac{1}{2}}$

$Br: 4s^2 4p^5 \rightarrow 4p^1$

          $L = 1$, $S = \frac{1}{2}$, $J = \frac{3}{2}, \frac{1}{2}$ $^2P_{\frac{3}{2}}$

16. $_{44}R_u$ 可推测：由于电子数44，可能组态 $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^6 5s^2$ A

或 $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^7 5s^1$ B

若为 A: 2   1   0   -1   -2   S=2   L=2

          J=4,3,2,1,0 $^5D_4$

若为 B: 2   1   0   -1   -2   0   S=2   L=3
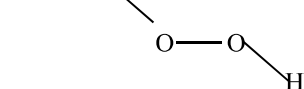
          J=5,4,3,2,1 $^5F_5$

所以 Ru 基组态应为 B: $1s^2 2s^2 2p^6 3s^2 3p^6 3d^{10} 4s^2 4p^6 4d^7 5s^1$
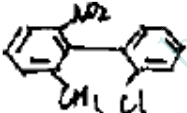
第三章

2. HCN： c_∞, σ_v

CO₂： 直线型分子： $E, i, c_\infty, c_2, \sigma_d, \sigma_h$

H₂O₂： H c_2, E

C₂H₄： $E, i, 3c_2, 2\sigma_d, \sigma_h$

C_6H_6: $E, i, c_6 + 6c_2, \sigma_h + 6\sigma_d$

4.

分子	分子点群	偶极矩	旋光性
（1） CH_2Cl_2	c_{2v}	有	无
（2） $CH_2 = CH - CH = CH_2$	c_{2h}	无	无
（3） OCS	$c_{\infty v}$	有	无
（4） IF_7	D_{5h}	无	无
（5） CH_4	T_d	无	无
（6） B_2H_6	D_{2h}	无	无
（7） H_3BO_3	C_{3h}	无	无
（8） S_8	D_{4d}	无	无
（9）	C_s	有	无
（10） $Fe(C_5H_4Cl)_2$	C_i	无	无
（11）	C_s	有	无
（12）	C_i	有	有

5. C_{3v}：$\{E, C_3, C_3^*, \sigma_v^{(1)}, \sigma_v^{(2)}, \sigma_v^{(3)}\}$ h=6

（1）子群 $\{E\}$ $g_1 = 1$ $\dfrac{6}{1} = 6$

           $\{E, C_3, C_3^2\}$ $g_2 = 3$ $\dfrac{6}{3} = 2$

           $\{E, \sigma_v^{(1)}\}$ $g_3 = 2$ $\dfrac{6}{2} = 3$

（2）根据相似变换：C_{3v} 群分成三个共轭类 $\{E\}, \{C_3, C_3^2\}, \{\sigma_v^{(1)}, \sigma_v^{(2)}, \sigma_v^{(3)}\}$

     H=6   元素数目：1,   2,   3

$$6\!\!\!/1 = 6 \qquad 6\!\!\!/3 = 2 \qquad 6\!\!\!/2 = 3$$

6. C_{3v} 群的不可约表示及特征标为

C_{3v}	E	$2C_3$	$3\sigma_v$
A_1	1	1	1
A_2	1	1	-1
E	2	-1	0

（1）C_{3v} 有 3 个共轭类

   3 个不可约表示

（2）维数：A_1 为 1 维，A_2 为 1 维，E 为 2 维，$1^2 + 1^2 + 2^2 = 6$

（3）不可约表示为：A_1：$1^2 + 1^2 \times 2 + 1^2 \times 3 = 6$ C_{3v} 阶：h=6

   A_2：$1^2 + 1^2 \times 2 + (-1)^2 \times 3 = 6$

   E：$2^2 + (-1)^2 \times 2 + 0^2 \times 3 = 6$

（4）以 A_2 和 E 为例：i，j 均为 E 时，i=j

$$x_E(E) = 2, x_E(C_3) = -1, x_E(\sigma_v) = 0$$

所以 $\dfrac{1}{6}[2 \times 2 + (-1)(-1) + (-1)(-1) + 0 \cdot 0 + 0 \cdot 0 + 0 \cdot 0] = 1$
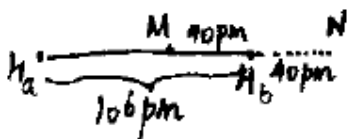
I 为 E 表示，j 为 A_2 表示时，$i \neq j$

E 表示中：$x_E(E) = 2, x_E(C_3) = 1, x_E(\sigma_v) = 1$

A_2 表示中：$x_E(E) = 1, x_E(C_3) = -1, x_E(\sigma_v) = 0$

$$\dfrac{1}{6}[2 \times 1 + 1 \times (-1) + 1 \times (-1) + 1 \cdot 0 + 1 \cdot 0 + 1 \cdot 0] = 0$$

同理，其它不可约表示之间也满足正交归一性

第四章

9.

$$\psi_{\sigma_{1s}} = \frac{1}{\sqrt{2+2S_{ab}}}(\phi_a + \phi_b) = c(e^{-\frac{r_a}{a_0}} + e^{-\frac{r_b}{a_0}})$$

$$c = \frac{1}{\sqrt{\pi a_0^3}} \cdot \frac{1}{\sqrt{2+2S_{ab}}}$$

M 点：$r_a = 66pm, r_b = 40pm$ $\psi_M^2 = c^2(e^{-\frac{66}{52.9}} + e^{-\frac{40}{52.9}})$

N 点：$r_a = 146pm, r_b = 40pm$ $\psi_N^2 = c^2(e^{-\frac{146}{52.9}} + e^{-\frac{40}{52.9}})$

$$\frac{\psi_M^2}{\psi_N^2} = 1.42$$

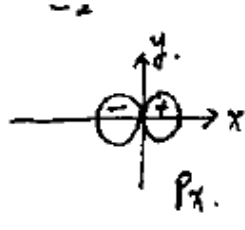M 处于两核之间，N 位于核的外侧，在 M 点电子出现的概率密度为 N 点的 1.42 倍
说明在成键轨道中，电子趋于两核之间，有拉紧两核的趋势

10. $\phi = c_1\phi_1 + c_2\phi_2$

根据变分原理：$\overline{E} = \dfrac{c_1^2 H_{11} + 2c_1c_2 H_{12} + c_2^2 H_{22}}{c_1^2 S_{11} + 2c_1c_2 S_{12} + c_2^2 S_{22}}$

令 $\overline{E}$ 取极小值，$\dfrac{\partial \overline{E}}{\partial c_1} = 0$，$\dfrac{\partial \overline{E}}{\partial c_2} = 0$ 得久期方程组

$$\begin{cases} c_1(H_{11} - E_s S_{11}) + c_2(H_{12} - E_s S_{12}) = 0 \\ c_1(H_{12} - E_s S_{12}) + c_2(H_{22} - E_s S_{22}) = 0 \end{cases}$$

由第一式 $\dfrac{c_1}{c_2} = -\dfrac{H_{12} - E_s S_{12}}{H_{11} - E_s S_{11}}$

12.
两者重叠 Sab=0，不能组成有效的分子轨道

13. $O_2 : 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^2$ 键级 2

$O_2^+ : 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^1$ 键级 2.5

$O_2^- : 1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^3$ 键级 1.5

键长：$O_2^- > O_2 > O_2^+$　　键能：$O_2^- < O_2 < O_2^+$　键级越小化学键越弱，键长越长

16. 令 $\psi = C_a \phi_a + C_b \phi_b$

由于 $\int \psi^* \psi d\tau = 1 \Rightarrow \int (C_a \phi_a + C_b \phi_b)^* (C_a \phi_a + C_b \phi_b) d\tau = 1$

$\Rightarrow C_a^2 \int \phi_a^* \phi_a d\tau + C_b^2 \int \phi_b^* \phi_b d\tau + C_a C_b \int \phi_a^* \phi_b d\tau + C_a C_b \int \phi_b^* \phi_a d\tau = 1$

由于忽略原子轨道的重叠：$\int \phi_a^* \phi_b d\tau = \int \phi_b^* \phi_a d\tau = 0$

上式变为：$C_a^2 + C_b^2 = 1$　　$C_a^2 \Big/ C_b^2 = \dfrac{90\%}{10\%} = 9$

$\Rightarrow C_a = \pm\sqrt{\dfrac{9}{10}}$　　$C_b = \pm\sqrt{\dfrac{1}{10}}$　　$\psi = \sqrt{\dfrac{9}{10}}\phi_a \pm \sqrt{\dfrac{1}{10}}\phi_b$

17. N_2^+：$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^1$　　键级=2.5

F_2^+：$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^3$　　键级=1.5

N_2^{2-}：$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2 1\pi_g^2$　　键级=2

F_2^{2-}：$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^4 3\sigma_u^2$　　键级=0

H_2：$1\sigma_g^2$　　反磁性

O_2^+：$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^1$　　顺磁性

N_2：$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 1\pi_u^4 3\sigma_g^2$ 反磁性

CO：$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2$　反磁性

18. $^1H^{35}Cl$：$\mu = \dfrac{M_1 M_2}{M_1 + M_2} \times \dfrac{10^{-3}}{N_A} = \dfrac{1 \times 35}{1 + 35} \times \dfrac{10^{-3}}{6.02 \times 10^{23}} = 1.61 \times 10^{-27} kg$

$I = \mu R^2 = 1.61 \times 10^{-27} \times (127.46 \times 10^{-12})^2 = 2.62 \times 10^{-47} kg \cdot m^2$

同理求得 $^2H^{35}Cl$：$\mu = 3.14 \times 0^{-27} kg$　$I = 5.10 \times 10^{-47} kg \cdot m^2$

同理求得 $^1H^{37}Cl$：$\mu = 1.62 \times 10^{-27} kg$　$I = 2.63 \times 10^{-47} kg \cdot m^2$

同理求得 $^2H^{37}Cl$：$\mu = 3.15 \times 10^{-27} kg$　$I = 5.12 \times 10^{-47} kg \cdot m^2$

19. $^{12}C^{16}O$ $\mu = \frac{12 \times 16}{12 + 16} \times \frac{10^{-3}}{6.02 \times 10^{23}} = 1.1387 \times 10^{-26} kg$

$B = \frac{h}{8\pi^2 Ic} = \frac{h}{8\pi^2 \mu r^2 c} = \frac{6.626 \times 10^{-34}}{8 \times 3.14^2 \times 1.1387 \times 10^{-26} \times \left(112.82 \times 10^{-12}\right)^2 \times 3 \times 10^8} = 1.93 cm^{-1}$

$\widetilde{v}(J) = 2B(J+1)$

$\widetilde{v}_{0 \to 1} = 2B = 3.86 cm^{-1}$ $\qquad$ $\widetilde{v}_{1 \to 2} = 4B = 7.72 cm^{-1}$ $\qquad$ $\widetilde{v}_{2 \to 3} = 6B = 11.58 cm^{-1}$

$\widetilde{v}_{3 \to 4} = 8B = 15.44 cm^{-1}$

$^{13}C^{16}O$ $\mu^1 = \frac{13 \times 16}{13 + 16} \times \frac{10^{-3}}{6.02 \times 10^{23}} = 1.1910 \times 10^{-26} kg$ $B^{'} = 1.85 cm^{-1}$

$^{13}C^{16}O$的前几条谱线波数分别为：$2B^1, 4B^1, 6B^1, 8B^1 \cdots$

而$\left(2B - 2B^{'}\right)$是$\left(2B - 2B^{'}\right), \left(4B - 4B^{'}\right), \left(6B - 6B^{'}\right) \cdots$中差值最小的

$2B - 2B^{'} = 3.86 - 2 \times 1.85 = 0.16 cm^{-1}$

所以仪器分辨率至少大于$0.16 cm^{-1}$才能将$^{12}C^{16}O$与$^{13}C^{16}O$的谱线区分开

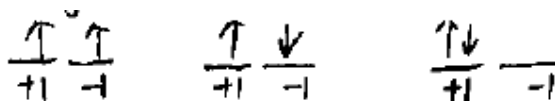20. CO：基态$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2$闭壳层 $\wedge = 0$ $S = 0$ $^1\sum^+$ 键级为3

第一激发态：$1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^1 2\pi^1$ 键级为2

$\Lambda = |0 + 1| = 1$ $S = \left|\sum M_{S_i}\right| = \left|\frac{1}{2} + \frac{1}{2}\right| = 1$ $^3\Pi$

或$S = \left|\sum M_{S_i}\right| = \left|\frac{1}{2} - \frac{1}{2}\right| = 0$ $^1\Pi$

O_2：基态：$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^2$

考虑开壳层$1\pi_g^2$ 键级为2

电子占据

$\Lambda = \left|\sum_i M_i\right| = 0$ $\qquad\qquad$ 0 $\qquad\qquad\qquad$ 2

$$S = \left|\sum_i M_{S_i}\right| = 1 \qquad\qquad 0 \qquad\qquad 0$$

电子谱项 $^3\Sigma_g^-$ $\qquad\qquad$ $^1\Sigma_g^+$ $\qquad\qquad$ $^1\Delta_g$

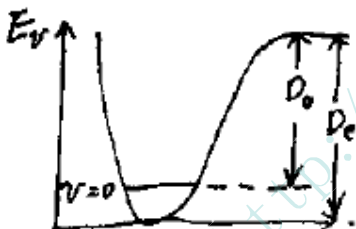第一激发态：$1\sigma_g^2 1\sigma_u^2 2\sigma_g^2 2\sigma_u^2 3\sigma_g^2 1\pi_u^4 1\pi_g^1 3\sigma_u^1$ 键级为2

考虑 $1\pi_g^1 3\sigma_u^1$

$$\Lambda = \left|\sum_i M_i\right| = |0+1| = 1 \quad S = 0,1 \; ^3\Pi, ^1\Pi$$

23. $\omega_e = \dfrac{\nu}{c} = \dfrac{1}{2\pi c}\sqrt{\dfrac{k_e}{\mu}}$ 同位素效应不影响化学键性质，所以 H_2, HD, D_0 的 k_e 相等

$$\omega_{eHD} = \omega_{eH_2}\cdot\sqrt{\frac{\mu_{H_2}}{\mu_{HD}}} = 4.4\times10^5\times\sqrt{\frac{1/2}{2/3}} = 3.815\times10^5\,(m^{-1})$$

$$\omega_{eD_2} = \omega_{eH_2}\cdot\sqrt{\frac{\mu_{H_2}}{\mu_{D_2}}} = 4.4\times10^5\times\sqrt{\frac{1/2}{4/4}} = 3.115\times10^5\,(m^{-1})$$

$D_e = D_0 + \frac{1}{2}h\nu_0 = D_0 + \frac{1}{2}h\omega_e c$ 由于 H_2 和 D_2 化学键相同，势能曲线一定相同，

故 $D_e^{H_2} = D_e^{D_2}$

$$D_0^{H_2} + \frac{1}{2}h\omega_{eH_2}c = D_0^{D_2} + \frac{1}{2}h\omega_{eD_2}c$$

$$D_0^{D_2} = D_0^{H_2} - \frac{1}{2}hc(\omega_{eD_2} - \omega_{eH_2}) = \frac{4.31\times10^2\times10^3}{6.02\times10^{23}} - \frac{1}{2}\times6.626\times10^{-34}\times3\times10^8(3.115-4.4)\times10^5$$

$$= 7.16\times10^{-19} + 1.27\times10^{-20} = 7.29\times10^{-19}\,J = 7.29\times10^{-19}\times10^{-3}\times6.02\times10^{23} = 438.9\,(KJ\cdot mol^{-1})$$

补充材料：变分法证明：对于 $\hat{H}$，存在任意归一化品优波函数 ϕ，则有 $\overline{E} = \dfrac{\int \phi*\hat{H}\phi d\tau}{\int \phi*\phi d\tau} \geq E_0$

证明：将 $\hat{H}$ 对应的一组正交归一完备的本征态记为 $\{\psi_0, \psi_1, \cdots \psi_i, \cdots\}$，相应的本征值为

$\{E_0, E_1, \cdots E_i, \cdots\}$ 且 $E_0 \le E_1 \le E_2 \cdots$，则 $\hat{H}\psi_i = E_i\psi_i (i = 0,1,2,\cdots)$

有一试探函数 ϕ，由本征函数系的完备性，则 $\phi = \sum_i a_i\psi_i$

$$Y \cong \int \phi * \hat{H}\phi d\tau = \int \left(\sum_i a_i\psi_i\right) * \hat{H}\left(\sum_j a_j\psi_j\right) d\tau$$

则有 $= \sum_i \sum_j a_i^* a_j \int \psi_i^* \hat{H}\psi_j d\tau = \sum_i \sum_j a_i^* a_j \int \psi_i^* E_j \psi_j d\tau = \sum_i \sum_j a_i^* a_j E_j \delta_{ij}$

$$= \sum_i |a_i|^2 E_i = E_0\left(\sum_i |a_i|^2 \frac{E_i}{E_0}\right)$$

$$Z = \int \phi * \phi d\tau = \int \left(\sum_i a_i\psi_i\right) * \left(\sum_j a_j\psi_j\right) d\tau$$

$$= \sum_i \sum_j a_i^* a_j \int \psi_i^* \psi_j d\tau = \sum_i \sum_j a_i^* a_j \delta_{ij} = \sum_i |a_i|^2$$

$$\therefore \langle H \rangle = \overline{E} = \frac{Y}{Z} = \frac{E_0\left(\sum_i |a_i|^2 \cdot \frac{E_i}{E_0}\right)}{\sum_i |a_i|^2} \ge E_0$$

第五章

10. $\Phi_k = \sqrt{\alpha_k}\phi_s + \sqrt{\beta_k}\phi_{p_k}$ $\Phi_{p_k} = \sqrt{\frac{1}{\beta_k}}\left(C_{kx}\phi_{p_x} + C_{ky}\phi_{p_y} + C_{kz}\phi_{p_z}\right)$

（1）sp：等性杂化 $n_1 = n_2 = 1$，$\cos\theta = -1$ $\theta = 180°$ $\alpha = \frac{1}{2}$ $\beta = \frac{1}{2}$

有个轨道指向 x 轴：$\phi_{P_1} = \phi_{p_x}$

$\phi_1 = \sqrt{\alpha}\phi_s + \sqrt{\beta}\phi_{P_1} = \sqrt{\frac{1}{2}}\left(\phi_s + \phi_{p_x}\right)$

（2）sp^2：$n_1 = n_2 = n_3 = 2$，$\alpha = \frac{1}{3}$ $\beta = \frac{2}{3}$

$\phi_{P_1} = \phi_{p_x}$

$\phi_1 = \sqrt{\alpha}\phi_s + \sqrt{\beta}\phi_{P_1} = \sqrt{\frac{1}{3}}\phi_s + \sqrt{\frac{2}{3}}\phi_{p_x}$

（3）sp^3：$n_1 = n_2 = n_3 = n_4 = 3$，$\alpha = \frac{1}{4}$ $\beta = \frac{3}{4}$

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$$\phi_{P_1} = \phi_{p_x}$$

$$\phi_1 = \sqrt{\alpha}\phi_s + \sqrt{\beta}\phi_{P_1} = \frac{1}{2}\phi_s + \sqrt{\frac{3}{4}}\phi_{p_x}$$
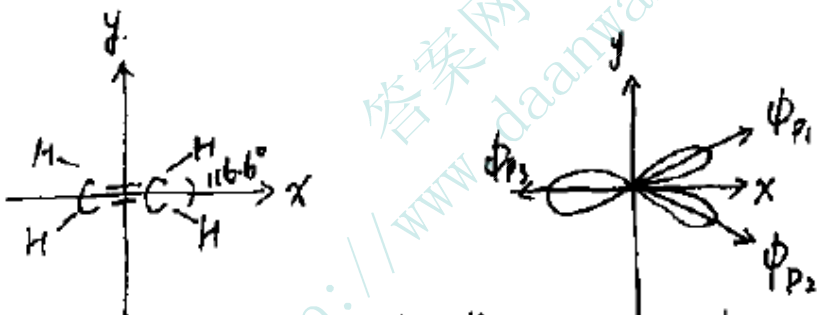
11. $f = \sqrt{\alpha} + \sqrt{3\beta}$

$sp : \alpha = \frac{1}{2}, \beta = \frac{1}{2}$ $f_{sp} = \sqrt{\frac{1}{2}} + \sqrt{\frac{3}{2}} = 1.932$ $f_s = 1$

$sp^2 : \alpha = \frac{1}{3}, \beta = \frac{2}{3}$ $f_{sp^2} = \sqrt{\frac{1}{3}} + \sqrt{2} = 1.992$ $f_p = 1.732$

$sp^3 : \alpha = \frac{1}{4}, \beta = \frac{3}{4}$ $f_{sp^3} = \sqrt{\frac{1}{4}} + \sqrt{\frac{9}{4}} = 2$

成键能力：$s < p < sp < sp^2 < sp^3$

12.

根据乙炔性质，$C-H$ 键长完全相同，可知 ϕ_{P_1} 与 ϕ_{P_2} 是等性杂化轨道

$\cos\theta_{12} = -\frac{1}{n} \Rightarrow n = -\frac{1}{\cos 116.6°} = 2.23$ 所以1，2轨道是 $sp^{2.23}$

$\cos\theta_{13} = -\frac{1}{\sqrt{n_1 n_3}} = -\frac{1}{\sqrt{2.23 n_3}} = \cos\frac{360-116.6}{2} \Rightarrow n_3 = \frac{1}{2.23 \cdot \cos^2 121.7} = 1.62$

$\frac{\beta_3}{\alpha_3} = 1.62$ $\alpha_3 + \beta_3 = 1 \Rightarrow \alpha_3 = 0.38$ $\beta_3 = 0.62 \Rightarrow$

由于 ϕ_{P_3} 在 x 轴反方向，$\phi_{P_3} = -\phi_{p_x}$ $\therefore \phi_3 = \sqrt{0.38}\phi_s - \sqrt{0.62}\phi_{p_x}$

对于 $n_1 = n_2 = 2.23$，$\frac{\beta_1}{\alpha_1} = 2.23$ $\alpha_1 + \beta_1 = 1 \Rightarrow \alpha_1 = 0.31$ $\beta_1 = 0.69$ 同理 $\alpha_2 = 0.31$

$\beta_2 = 0.69$

$$\phi_{p_2} = \sqrt{\frac{1}{0.69}}\left(C_{2x}\phi_{p_x} + C_{2y}\phi_{p_y}\right) \quad \phi_{p_1} = \sqrt{\frac{1}{0.69}}\left(C_{1x}\phi_{p_x} + C_{1y}\phi_{p_y}\right)$$

令 ϕ_{p_2}, ϕ_{p_1} 归一化，由于 ϕ_{p_1} 在 y 轴上投影为正，ϕ_{p_2} 在 y 轴投影为负

$$\left(\sqrt{\frac{1}{0.69}}C_{2x}\right)^2 + \left(\sqrt{\frac{1}{0.69}}C_{2y}\right)^2 = 1 \quad \frac{C_{2y}}{C_{2x}} = tg\frac{116.6}{2} \Rightarrow C_{2x} = 0.44, C_{2y} = -0.71$$
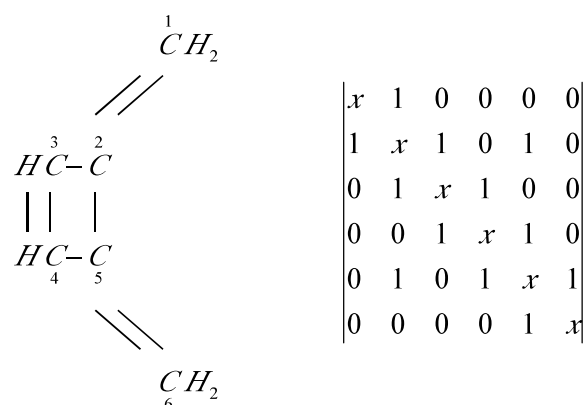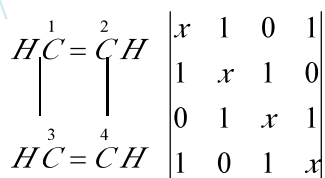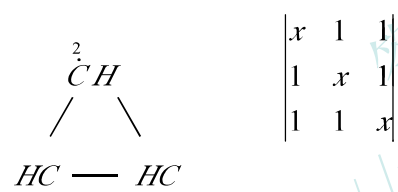
$$\left(\sqrt{\frac{1}{0.69}}C_{1x}\right)^2 + \left(\sqrt{\frac{1}{0.69}}C_{1y}\right)^2 = 1 \quad \frac{C_{1y}}{C_{1x}} = tg\frac{116.6}{2} \Rightarrow C_{1x} = 0.44, C_{1y} = 0.71$$
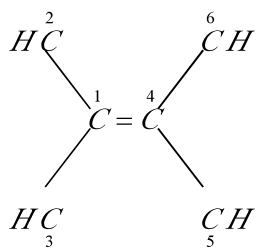
$$\therefore \phi_1 = \sqrt{0.31}\phi_s + \sqrt{0.69}\phi_{p_1} = \sqrt{0.31}\phi_s + 0.44\phi_{p_x} + 0.71\phi_{p_y}$$

$$\phi_2 = \sqrt{0.31}\phi_s + 0.44\phi_{p_x} - 0.71\phi_{p_y}$$

$$\phi_3 = \sqrt{0.38}\phi_s - \sqrt{0.62}\phi_{p_x}$$

17. $H_2\overset{1}{C}=\overset{2}{C}H_2 \quad \begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix}$ $\qquad H_2C=CH-CH_2 \quad \begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix}$

$\overset{2}{C}H$
／ ＼
$HC \;\overline{=\!=}\; HC$

$\begin{vmatrix} x & 1 & 1 \\ 1 & x & 1 \\ 1 & 1 & x \end{vmatrix}$

$H\overset{1}{C}=\overset{2}{C}H$
｜ ｜
$H\overset{3}{C}=\overset{4}{C}H$

$\begin{vmatrix} x & 1 & 0 & 1 \\ 1 & x & 1 & 0 \\ 0 & 1 & x & 1 \\ 1 & 0 & 1 & x \end{vmatrix}$

$\overset{1}{C}H_2$
／／
$H\overset{3}{C}-\overset{2}{C}$
｜｜ ｜
$H\overset{}{C}-\overset{}{C}$
4   5
＼＼
$\underset{6}{C}H_2$

$\begin{vmatrix} x & 1 & 0 & 0 & 0 & 0 \\ 1 & x & 1 & 0 & 1 & 0 \\ 0 & 1 & x & 1 & 0 & 0 \\ 0 & 0 & 1 & x & 1 & 0 \\ 0 & 1 & 0 & 1 & x & 1 \\ 0 & 0 & 0 & 0 & 1 & x \end{vmatrix}$

$$H\overset{2}{C}\qquad\qquad\overset{6}{C}H$$
$$\overset{1}{C}=\overset{4}{C}$$
$$H\underset{3}{C}\qquad\qquad\underset{5}{C}H$$

$$\begin{vmatrix} x & 1 & 1 & 1 & 0 & 0 \\ 1 & x & 1 & 0 & 0 & 0 \\ 1 & 1 & x & 0 & 0 & 0 \\ 1 & 0 & 0 & x & 1 & 1 \\ 0 & 0 & 0 & 1 & x & 1 \\ 0 & 0 & 0 & 1 & 1 & x \end{vmatrix}$$

18.（1）$CH_2 = CH - CH_2$

离域：$\begin{vmatrix} x & 1 & 0 \\ 1 & x & 1 \\ 0 & 1 & x \end{vmatrix} = 0 \Rightarrow x = 0, x = \pm\sqrt{2} \Rightarrow$

$E_1 = \alpha + \sqrt{2}\beta$

$E_2 = \alpha$ $\qquad\qquad E_{D\pi} = 2E_1 + E_2 = 3\alpha + 2\sqrt{2}\beta$

$E_3 = \alpha - \sqrt{2}\beta$

定域：$\begin{vmatrix} x & 1 \\ 1 & x \end{vmatrix} = 0 \Rightarrow x = \pm 1 \Rightarrow \begin{matrix} E_1 = \alpha + \beta \\ E_2 = \alpha - \beta \end{matrix} \quad E_{L\pi} = 2E_1 + \alpha = 3\alpha + 2\beta$

$DE_\pi = E_{D\pi} - E_{L\pi} = 2(\sqrt{2} - 1)\beta$

（2）$\left[CH_2 = CH - CH_2 \right]^+$

$E_{D\pi} = 2E_1 = 2\alpha + 2\sqrt{2}\beta$，$E_{L\pi} = 2\alpha + 2\beta$ $\quad DE_\pi = 2\left(\sqrt{2} - 1\right)\beta$

(3) $E_{D\pi} = 2E_1 + 2E_2 = 4\alpha + 2\sqrt{2}\beta$ $\quad E_{L\pi} = 4\alpha + 2\beta$

$DE_\pi = 2\left(\sqrt{2} - 1\right)\beta$

20. $\overset{1}{C} = \overset{2}{C} - \overset{3}{C} = \overset{4}{C}$ $\quad \psi_1^2 \psi_2^1 \psi_3^1$ 第一激发态

$q_{11} = 2C_{11}^2 + C_{21}^2 + C_{31}^2 = 2 \times 0.3717^2 + 0.6015^2 + 0.6015^2 = 1.000$

$q_{12} = 2C_{12}^2 + C_{22}^2 + C_{32}^2 = 2 \times 0.6015^2 + 0.3717^2 + (-0.3717)^2 = 1.000$

$q_{13} = 2C_{13}^2 + C_{23}^2 + C_{33}^2 = 2 \times 0.6015^2 + (-0.3717)^2 + (-0.3717)^2 = 1.000$

$$q_{14} = 2C_{14}^2 + C_{24}^2 + C_{34}^2 = 2 \times 0.3717^2 + (-0.6015)^2 + (0.6015)^2 = 1.000$$

$$P_{12} = 2C_{11}C_{12} + C_{21}C_{22} + C_{31}C_{32} = 2 \times 0.3717 \times 0.6015 + 0.6015 \times 0.3717 + 0.6015 \times (-0.3717) = 0.447$$

$$P_{23} = 2C_{12}C_{13} + C_{22}C_{23} + C_{32}C_{33} = 2 \times 0.6015 \times 0.6015 + 0.3717 \times (-0.3717) + (-0.3717) \times (-0.3717) = 0.723$$

$$P_{34} = 2C_{13}C_{14} + C_{23}C_{24} + C_{33}C_{34} = 2 \times 0.6015 \times 0.3717 + (-0.3717) \times (-0.6015) + (-0.3717) \times (0.6015) = 0.447$$

考虑 σ 键：总键级为 $P_{12} = 1.447$，$P_{23} = 1.723$，$P_{34} = 1.447$

$$N_1 = 2 + 1.447 = 3.447 \quad N_2 = 1 + P_{12} + P_{23} = 4.170 \quad N_3 = 1 + P_{23} + P_{34} = 4.170$$

$$N_4 = 2 + 1.447 = 3.447$$

$$\therefore F_1 = F_4 = 4.732 - 3.447 = 1.285 \quad F_2 = F_3 = 4.732 - 4.170 = 0.562$$

1.285 0.562

↑   ↑

$$CH_2 - CH \overset{1.723}{-} \underset{1.000}{C} H \overset{1.447}{-} \underset{1.000}{C} H_2$$

23. （1）$hv = g_N \mu_N B_\circ$

$$v = 100 MHz : B_0 = \frac{hv}{g_N \mu_N} = \frac{6.626 \times 10^{-34} \times 100 \times 10^6}{5.6857 \times 5.051 \times 10^{-27}} = 2.307(T)$$

$$v = 150 MHz : B_0 = \frac{6.626 \times 10^{-34} \times 150 \times 10^6}{5.6857 \times 5.051 \times 10^{-27}} = 3.461(T)$$
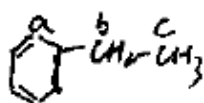
$$v = 200 MHz : B_0 = \frac{6.626 \times 10^{-34} \times 200 \times 10^6}{5.6857 \times 5.051 \times 10^{-27}} = 4.614(T)$$
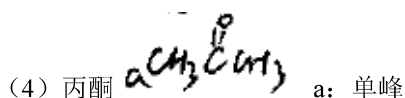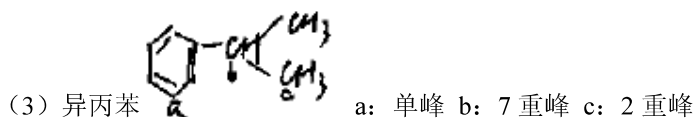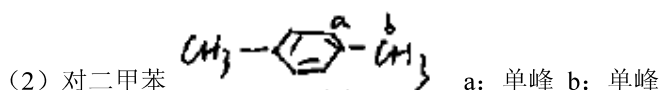
（2）$hv = g_e \mu_B B_0$

$$B_0 = 0.5T \quad v = \frac{g_e \mu_B B_0}{h} = \frac{2.0023 \times 9.274 \times 10^{-24} \times 0.5}{6.626 \times 10^{-34}} = 1.40 \times 10^{10}(Hz)$$

$$B_0 = 1.0T \quad v = \frac{2.0023 \times 9.274 \times 10^{-24} \times 1.0}{6.626 \times 10^{-34}} = 2.80 \times 10^{10}(Hz)$$

$$B_0 = 1.5T \quad v = 4.20 \times 10^{10}(Hz)$$

24. （1）乙苯 ：a：单峰 b：4 重峰 c：3 重峰

（2）对二甲苯 $CH_3-\langle\rangle-CH_3$ a：单峰 b：单峰

（3）异丙苯   a：单峰 b：7 重峰 c：2 重峰

（4）丙酮 $aCH_3\overset{O}{\overset{\|}{C}}CH_3$ a：单峰

第六章

6. 水是弱场配体，故 $Mn(H_2O)_6^{3+}$ 为高自旋，其 d 电子排布 $(t_{2g})^3(e_g)^1$

$$CFSE = 0 - \left[3 \times (-4D_q) + 6D_q\right] = 6D_q$$

处于 e_g 上电子失去后 $(t_{2g})^3$，$CFSE = 0 - \left[3 \times (-4D_q)\right] = 12D_q$

晶体场稳定化能增大，而且 $(t_{2g})^3(e_g)^1$ 也容易发生畸变

对于 $Cr(H_2O)_6^{3+}$：d 电子排布 $(t_{2g})^3(e_g)^0$，$CFSE = 12D_q$，这种排布很稳定，也不会发生畸变。

7. 因为两个配合物配体相同，NH_3 为光谱序列的中间位置，Δ_o 与中心离子的价态有关，

显然 $\Delta_{Co^{3+}} > \Delta_{Co^{2+}}$，而电子成对能基本不变，所以对于 $\left[Co(NH_3)_6\right]^{2+}：\Delta_o < p$，
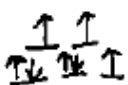
$\left[Co(NH_3)_6\right]^{3+}：\Delta_o > p$

Co^{2+} 的 d^7 有两种可能排布

$(t_{2g})^5(e_g)^2$：$CFSE_1 = 2p - \left[5 \times (-4D_q) + 2 \times 6D_q + 2p\right] = 8D_q$

$(t_{2g})^6(e_g)^1$：$CFSE_2 = 2p - \left[6 \times (-4D_q) + 6D_q + 3p\right] = 18D_q - p$

$CFSE_1 - CFSE_2 = p - 10D_q = p - \Delta_o > 0$ 第一种排法取得稳定能大

所以采用第一种排法高自旋，⬆⬇ ⬆⬇ ⬆   顺磁性

Co^{3+} 的 d^6 也有两种可能排布

$(t_{2g})^4(e_g)^2$：$CFSE_1 = p - \left[4 \times (-4D_q) + 2 \times 6D_q + p\right] = 4D_q$

$$(t_{2g})^6(e_g)^0: \quad CFSE_2 = p - \left[6 \times (-4D_q) + 3p\right] = 24D_q - 2p$$

$$CFSE_1 - CFSE_2 = 2p - 20D_q = 2(p - \Delta_o) < 0 \text{ 第二种排法取得稳定能大}$$

所以采用第二种排法低自旋，反磁性

9. Co^{2+}：d^7（F^-为弱场配体），高自旋，$(t_{2g})^5(e_g)^2$

$$CFSE = 2p - \left[5 \times (-4D_q) + 2 \times 6D_q + 2p\right] = 8D_q$$

Ni^{2+}：d^8 $(t_{2g})^6(e_g)^2$

$$CFSE = 0 - \left[3 \times (-4D_q) + 2 \times 6D_q\right] = 0$$

所以稳定化能从大到小的次序为：$[NiF_6]^{4-} > [CoF_6]^{4-} > [FeF_6]^{3-}$

10. Cu^{2+}：d^9 高自旋 $(t_{2g})^6(e_g)^3$ 大畸变

Co^{2+}：d^7 高自旋 $(t_{2g})^5(e_g)^2$ 小畸变

Fe^{3+}：d^5 低自旋 $(t_{2g})^5(e_g)^2$ 小畸变
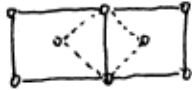
Ni^{2+}：d^8 低自旋 $(t_{2g})^6(e_g)^2$ 不畸变

$\therefore [Cu(H_2O)_6]^{2+} > [Co(H_2O)_6]^{2+} = [Fe(CN)_6]^{3-} > [Ni(CN)_6]^{4-}$
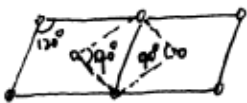
第七章

2. 正当格子的要求是：对称性高，点阵点少。

对于矩形：　　　　带心型式不可能用更高对称性或更少点阵点的格子来代替

若按虚线划出格子，违背了平移向量最好是 90° 的要求

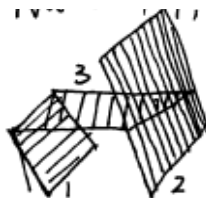对于正方形：　　　若有带心型式，按虚线连接后，格子仍为正方形，可点阵点少。故不可能存在正方形带心格子。

对于六方格子：　　同上，同理。带心六方可被矩形代替

对于平行四边形格子：　　同理，带心平行四边形可被简单平行四边形

代替

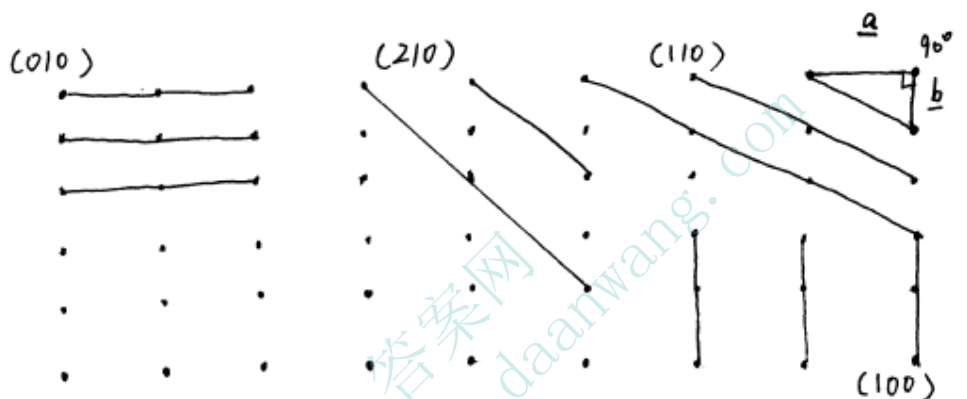5. 对于立方面心点阵型式符合立方晶系的对称性，从中不可能取出更小且对称性与原同的格子。只能取较小的菱面体。显然对称性降低了，所以立方面心格子存在。而四方面心格子可取出体积更小且对称类型相同的四方体心格子。故四方面心不存在。

9. 不论该晶体属于哪一个晶系，均为简单的空间点阵（p），结构基元为 AB

11. Na^+：4 个；Cl^-：4 个；NaCl：4 个

1：（101）2：（201）3：（001）

12.

立方晶系 a=b=c　　c 轴与纸面垂直，故不画出

夹角（100）—（010）：90°

　　　（100）—（110）：45°

　　　（100）—（210）：arctg(1/2)

21. 在面心结构中，每个晶胞含四个原子，其分数坐标为：

$(0,0,0)$　$(0,\frac{1}{2},\frac{1}{2})$　$(\frac{1}{2},\frac{1}{2},0)$　$(\frac{1}{2},0,\frac{1}{2})$

$$\left|F_{hkl}\right|^2 = [f\cos 2\pi(0\cdot h+0\cdot k+0\cdot l)+f\cos 2\pi(0\cdot h+\frac{k}{2}+\frac{l}{2})$$

$$+f\cos 2\pi(\frac{h}{2}+\frac{k}{2}+0\cdot l)+f\cos 2\pi(\frac{h}{2}+0\cdot k+\frac{l}{2})]^2$$

$$+[f\sin 2\pi(0\cdot h+0\cdot k+0\cdot l)+f\sin 2\pi(0\cdot h+\frac{k}{2}+\frac{l}{2})$$

$$+f\sin 2\pi(\frac{h}{2}+\frac{k}{2}+0\cdot l)+f\sin 2\pi(\frac{h}{2}+0\cdot k+\frac{l}{2})]^2$$

$$=f^2\left[1+\cos\pi(k+l)+\cos\pi(k+h)+\cos\pi(h+l)\right]^2$$

若 h,k,l 均为奇数或偶数时，$\left|F_{hkl}\right|^2=f^2(1+1+1+1)^2=16f^2$　k+l, h+k, h+l 均是偶数

若 h,k,l 奇偶混杂，则 k+l, h+k, h+l 中必有二奇一偶

则 $\left|F_{hkl}\right|^2 = f^2(1-1-1+1)^2 = 0$ 即系统消光。

$$\frac{1}{2}mv^2 = eV, \qquad p = mv = \sqrt{2meV}$$

$$\lambda = \frac{h}{\sqrt{2meV}} = \frac{6.6262 \times 10^{-34}}{\sqrt{2 \times 9.9095 \times 10^{-31} \times 1.6022 \times 10^{-19} \times 10^3}} \approx 0.3718 \times 10^{-10}\,m$$

$$\lambda = \frac{h}{mv} = \frac{6.6262 \times 10^{-34}}{10^{-10} \times 10^{-2}} = 6.6262 \times 10^{-22}\,m$$

$$E_n = \frac{n^2 h^2}{8ml^2} \qquad E_n \qquad E_{n-1} \qquad \Delta E_n = \frac{\left[n^2 - (n-1)^2\right]h^2}{8ml^2} = \frac{(2n-1)h^2}{8ml^2}$$

$$\lambda = \frac{hc}{\Delta E_n} = \frac{8ml^2 c}{(2n-1)h}$$

$$\lambda = \frac{8 \times 9.9095 \times 10^{-31} \times \left(5 \times 10^{-10}\right)^2 \times 2.9979 \times 10^8}{(2 \times 3 - 1) \times 6.6262 \times 10^{-34}} = 0.1793 \times 10^{-6}\,m$$

$$E_3 = \frac{3^2 \times \left(6.6262 \times 10^{-34}\right)^2}{8 \times 9.9095 \times 10^{-31} \times \left(5 \times 10^{-10}\right)^2} = 1.9938 \times 10^{-18}\,J$$

$$\lambda = \frac{E_3}{hc} = \frac{606262 \times 10^{-34} \times 2.9979 \times 10^8}{1.9938 \times 10^{-18}} = 0.9970 \times 10^{-7}\,m$$

$$E_n = -13.6\frac{Z^2}{n^2} = -13.6 \times \frac{1}{2^2} = -3.4\,J$$

$$|M| = \sqrt{l(l+1)}\hbar = \sqrt{2}\hbar$$

$$\cos\theta = \frac{m}{\sqrt{l(l+1)}} = 0$$

$$\therefore \theta = 90°$$

$$\psi_{2p_z} = \frac{1}{4\sqrt{2\pi a_0^3}}\left(\frac{r}{a_0}\right)e^{-\frac{r}{2a_0}}\cos\theta$$

$$L = \left|m_L\right| = \left|\sum_i m_{l_i}\right| = 1, \qquad S = \left|m_s\right| = \frac{1}{2}$$

$$m_l$$

↑	↑	

$I = 5 \times 10^{-10}$