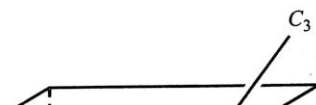


1. 配分: 一小題 1 分, 共 5 分 (1)4 (2)0 (3)3 (4)1 (5) 3

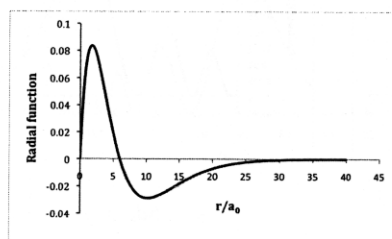
2. 配分: 一小題 2 分, 共 10 分

- p_x has $C_{\infty v}$ symmetry. (Ignoring the difference in sign between the two lobes, the point group would be $D_{\infty h}$.)
- d_{xy} has D_{2h} symmetry. (Ignoring the signs, the point group would be D_{4h} .)
- $d_{x^2-y^2}$ has D_{2h} symmetry. (Ignoring the signs, the point group would be D_{4h} .)
- d_{z^2} has $D_{\infty h}$ symmetry.
- f_{xyz} has T_d symmetry.

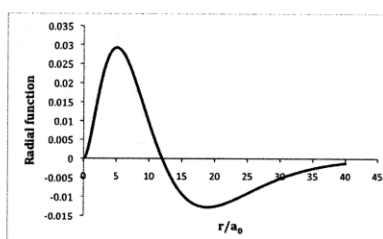


3. 配分: (a) 2 (b) 2 (c) 4 共 8 分

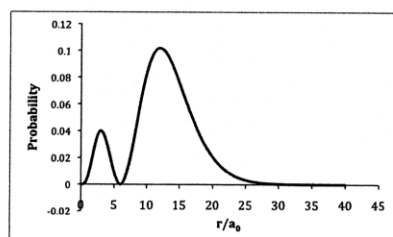
a. $3p_z$



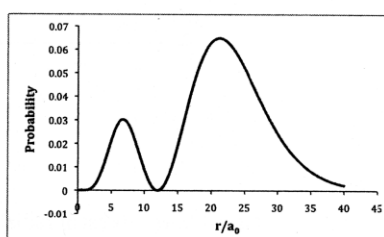
$4d_{xz}$



b. $3p_z$



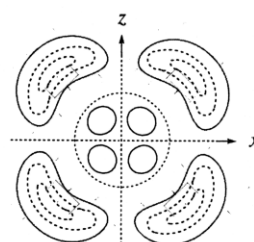
$4d_{xz}$



c. $3p_z$

For contour map, see Figure 2.8.

$4d_{xz}$



4.

$4f_{z(x^2-y^2)}$ orbital

- a. No radial nodes
- b. 3 angular nodes
- c. The angular nodes are solutions for $z(x^2-y^2) = 0$. These solutions are $z = 0$ (xy plane), and the planes where $x = y$ and $x = -y$, both perpendicular to the xy plane.
- d. There are 8 lobes, 4 above and 4 below the xy plane. Down the z axis, this orbital looks like a $d_{x^2-y^2}$ orbital, but the node at the xy plane splits each lobe in two. For an image of this orbital, please see <http://winter.group.shef.ac.uk/orbitron/> or another atomic orbital site on the Web.

4.配分: (a) 1 (b) 1 (c) 2 (d) 2 共 6 分

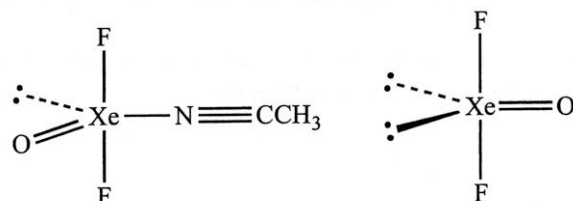
5.

配分:共 6 分	Sc	Ti	Compare with Ni
3d	1 分	1 分	1 分: Z^* of 3d = 4s (Sc) Different with Ni
4s	1 分	1 分	1 分: Z^* of 3d > 4s (Ti) Same with Ni The difference between 3d & 4s increases across the row of transition metals

	<u>Sc:</u>	<u>Ti:</u>
<u>3d electron:</u>		
1 Electron configuration	$(1s^2)(2s^2, 2p^6)(3s^2, 3p^6)(3d^1)(4s^2)$	$(1s^2)(2s^2, 2p^6)(3s^2, 3p^6)(3d^2)(4s^2)$
4a Contribution of other <i>d</i> electrons	None [only one electron in $(3d^1)$]	One other <i>3d</i> electron: Contribution to $S = 1 \times 0.35 = 0.35$
4b Contribution of electrons to left of $(3d^n)$	$18 \times 1.00 = 18.00$	$18 \times 1.00 = 18.00$
Total S	18.00	18.35
Z^*	$21 - 18.00 = 3.00$	$22 - 18.35 = 3.65$
<u>4s electron:</u>		
1 Electron configuration	$(1s^2)(2s^2, 2p^6)(3s^2, 3p^6)(3d^1)(4s^2)$	$(1s^2)(2s^2, 2p^6)(3s^2, 3p^6)(3d^2)(4s^2)$
3a Contribution of other $(4s^2)$ electron	Contribution to $S = 0.35$	Contribution to $S = 0.35$
3b Contribution of $(3s^2, 3p^6)(3d^n)$ electrons	$9 \times 0.85 = 7.65$	$10 \times 0.85 = 8.50$
3c Contribution of other electrons	$10 \times 1.00 = 10.00$	$10 \times 1.00 = 10.00$
Total S	$0.35 + 7.65 + 10.00 = 18.00$	$0.35 + 8.50 + 10.00 = 18.85$
Z^*	$21 - 18.00 = 3.00$	$22 - 18.85 = 3.15$

In Sc Slater's rules give the same value for the effective nuclear charge Z^* for the $3d$ and $4s$ electrons, consistent with the very similar energies of these orbitals. In Ti the effective nuclear charge is slightly less for $4s$ than for $3d$, by 0.50. This difference in the energies of $4s$ and $3d$ increases across the row of transition metals; by nickel, as calculated in the example in section 2.2.4, the $4s$ orbital has an effective nuclear charge 3.50 less than the $3d$ orbitals. This is consistent with the experimental observation that transition metal cations have electron configurations in which there are no valence s electrons; the $3d$ orbitals are lower in energy than the $4s$ orbital, so d orbitals are the ones that are occupied. A similar phenomenon is observed for the second and third row transition metals.

6. 配分:一題 2 分，共 4 分



In $\text{F}_2\text{O}(\text{Xe})\text{N}\equiv\text{CCH}_3$ the nitrogen–xenon bond is weak; see the reference for details on bond distances and angles.

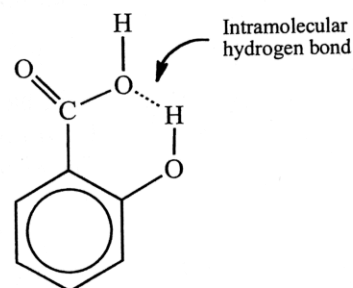
7. 配分:關鍵字(套粉紅色) or 圖示 or 描述完整

(a)1 (b) 1 (c) 2 (d) 1 (e) 2 (f) 1 (g) 2 共 10 分

a. The H–O bond of methanol is more polar than the H–S bond of methyl mercaptan. As a result, hydrogen bonding holds the molecules together and requires more energy for vaporization. The larger molecular weight of methyl mercaptan has a similar effect, but the hydrogen bonding in methanol has a stronger influence.

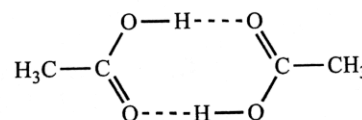
b. CO and N_2 have nearly identical molecular weights, but the polarity of CO leads to dipole–dipole attractions that help hold CO molecules together in the solid and liquid states.

c. The *ortho* isomer of hydroxybenzoic acid can form intramolecular hydrogen bonds, while the *meta* and *para* isomers tend to form dimers and larger aggregates in their hydrogen bonding. As a result of their better ability to form hydrogen bonds between molecules (*intermolecular* hydrogen bonds), the *meta* and *para* isomers have higher melting points (*ortho*, 159° ; *meta*, 201.3° ; *para*, $214\text{--}215^\circ$).

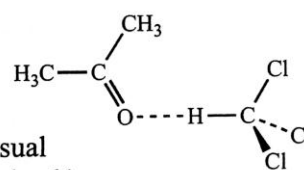


d. The London (dispersion) forces between atoms increase with the number of electrons, so the noble gases with larger Z have larger interatomic forces and higher boiling points.

e. Acetic acid can form hydrogen-bonded dimers in the gas phase, so the total number of particles in the gas is half the number expected by using the ideal gas law.



- f. Acetone has a negative carbonyl oxygen; chloroform has a positive hydrogen, due to the electronegative character of the chlorines. As a result, there is a stronger attraction between the different kinds of molecules than between molecules of the same kind, and a resulting lower vapor pressure. (This is an unusual case of hydrogen bonding, with no H-N, H-O, or H-F bond involved.)



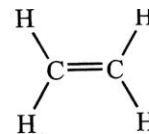
- g. CO has about 76 kJ contribution to its bond energy because of the electronegativity difference between C and O; attraction between the slightly positive and negative ends strengthens the bonding. Although this is not a complete explanation, it covers most of the difference between CO and N₂. In spite of its high bond energy, N₂ is thought by some to have some repulsion in its sigma bonding because of the short bond distance.

8.

配分: 共 15 分	Lewis structure	shape	Point group (最高對稱)
(a) <u>1+1+1</u> =3 分			C _{2v}
(b) <u>1+1+1</u> =3 分			C _s
(c) <u>1+1+1</u> =3 分			C _s
(d) <u>1+1+1</u> =3 分			D _{2d}
(e) <u>1+1+1</u> =3 分			Staggered: C _{2h} Eclipsed: C _{2v} Between: C ₂

9. 配分:每小題 2 分，共 10 分

- a. D_{2h} molecules have E , $C_2(z)$, $C_2(y)$, $C_2(x)$, i , $\sigma(xy)$, $\sigma(xz)$, and $\sigma(yz)$ operations.



b.

$$E: \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix} \quad C_2(z): \begin{vmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{vmatrix} \quad C_2(y): \begin{vmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{vmatrix}$$

$$C_2(x): \begin{vmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{vmatrix} \quad i: \begin{vmatrix} -1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & -1 \end{vmatrix} \quad \sigma(xy): \begin{vmatrix} 1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & -1 \end{vmatrix}$$

$$\sigma(xz): \begin{vmatrix} 1 & 0 & 0 \\ 0 & -1 & 0 \\ 0 & 0 & 1 \end{vmatrix} \quad \sigma(yz): \begin{vmatrix} -1 & 0 & 0 \\ 0 & 1 & 0 \\ 0 & 0 & 1 \end{vmatrix}$$

c.

	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$
χ	3	-1	-1	-1	-3	1	1	1

d.

Γ_1	1	-1	-1	1	-1	1	1	-1	matching B_{3u}
Γ_2	1	-1	1	-1	-1	1	-1	1	matching B_{2u}
Γ_3	1	1	-1	-1	-1	-1	1	1	matching B_{1u}

e. $\Gamma_1 \times \Gamma_2 = 1 \times 1 + (-1) \times (-1) + (-1) \times 1 + 1 \times (-1) + (-1) \times (-1) + 1 \times 1$
 $+ 1 \times (-1) + (-1) \times 1 = 0$

$$\Gamma_1 \times \Gamma_3 = 1 \times 1 + (-1) \times 1 + (-1) \times (-1) + 1 \times (-1) + (-1) \times (-1) + 1 \times (-1)$$

$$+ 1 \times 1 + (-1) \times 1 = 0$$

$$\Gamma_2 \times \Gamma_3 = 1 \times 1 + (-1) \times 1 + 1 \times (-1) + (-1) \times (-1) + (-1) \times (-1) + 1 \times (-1)$$

$$+ (-1) \times 1 + 1 \times 1 = 0$$

10. 配分:每小題 4 分共 12 分，

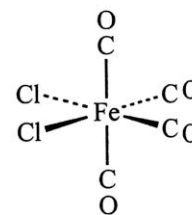
每小題 reducible representation: 2 分; reduce 結果(IR active):1 分

幾個 bands: 1 分(各自代表什麼 symmetry);

- a. *cis*-Fe(CO)₄Cl₂ has C_{2v} symmetry.

The vectors for CO stretching have the representation Γ below:

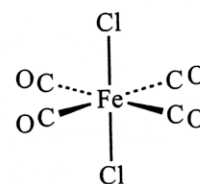
C _{2v}	E	C ₂	$\sigma_v(xz)$	$\sigma_v'(yz)$	
Γ	4	0	2	2	
A ₁	1	1	1	1	z
A ₂	1	1	-1	-1	
B ₁	1	-1	1	-1	x
B ₂	1	-1	-1	1	y



$$\begin{aligned}
 n(A_1) &= 1/4[4 \times 1 + 0 \times 1 + 2 \times 1 + 2 \times 1] = 2 \\
 n(A_2) &= 1/4[4 \times 1 + 0 \times 1 + 2 \times (-1) + 2 \times (-1)] = 0 \\
 n(B_1) &= 1/4[4 \times 1 + 0 \times (-1) + 2 \times 1 + 2 \times (-1)] = 1 \\
 n(B_2) &= 1/4[4 \times 1 + 0 \times (-1) + 2 \times (-1) + 2 \times 1] = 1 \\
 \Gamma &= 2 A_1 + B_1 + B_2, \text{ all four IR active.}
 \end{aligned}$$

- b. *trans*-Fe(CO)₄Cl₂ has D_{4h} symmetry.

D _{4h}	E	2C ₄	C ₂	2C _{2'}	2C _{2''}	i	2S ₄	σ_h	2 σ_v	2 σ_d	
Γ	4	0	0	2	0	0	0	4	2	0	
A _{2u}	1	1	1	-1	-1	-1	-1	-1	1	1	z
E _u	2	0	-2	0	0	-2	0	2	0	0	(x,y)



Omitting the operations that have zeroes in Γ :

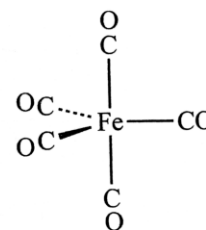
$$\begin{aligned}
 n(A_{2u}) &= 1/16[4 \times 1 + 2 \times 2 \times (-1) + 4 \times (-1) + 2 \times 2 \times 1] = 0 \\
 n(E_u) &= 1/16[4 \times 2 + 2 \times 2 \times 0 + 4 \times 2 + 2 \times 2 \times 0] = 1 \text{ (IR active)}
 \end{aligned}$$

Note: In checking for IR-active bands, it is only necessary to check the irreducible representations having the same symmetry as x, y, or z, or a combination of them.

- c. Fe(CO)₅ has D_{3h} symmetry.

The vectors for C–O stretching have the following representation Γ :

D _{3h}	E	2C ₃	3C ₂	σ_h	2S ₃	3 σ_v	
Γ	5	2	1	3	0	3	
E'	2	-1	0	2	-1	0	(x, y)
A _{2''}	1	1	-1	-1	-1	1	z



$$\begin{aligned}
 n(E') &= 1/12 [(5 \times 2) + (2 \times 2 \times -1) + (3 \times 2)] = 1 \\
 n(A_2'') &= 1/12 [(5 \times 1) + (2 \times 2 \times 1) + (3 \times 1 \times -1) + (3 \times -1) + (3 \times 3 \times 1)] = 1
 \end{aligned}$$

There are two bands, one matching E' and one matching A_{2''}. These are the only irreducible representations that match the coordinates x, y, and z.

11. 配分:O₂ M.O.--->4 分 解釋:2 分，共 6 分

12. 配分:(a) 4 (b) 4 (c)1 共 9 分

a. PCl₅ has D_{3h} symmetry.

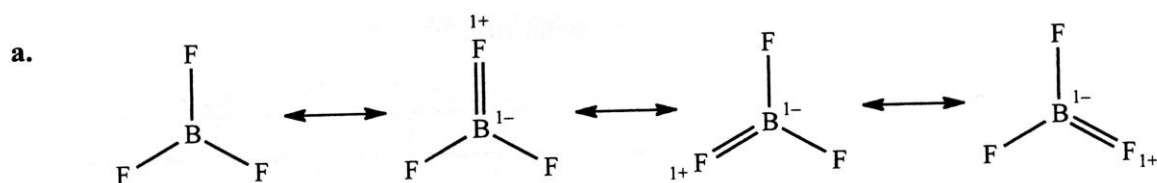
D _{3h}	E	2C ₃	3C ₂	σ _h	2S ₃	3σ _v	
Γ	5	2	1	3	0	3	(x, y) (x ² -y ² , xy)
E'	2	-1	0	2	-1	0	z ²
A ₁ '	1	1	1	1	1	1	z
A ₂ ''	1	1	-1	-1	-1	1	

Γ = E' + 2A₁' + A₂'', so the hybrids are dsp³ or d³sp.

b. This could also be analyzed separately for the axial and the equatorial positions. The p_z and d_z² orbitals can bond to the axial chlorines (A₁' + A₂'') and the s, p_x, and p_y orbitals or the s, d_x²-y², and d_{xy} orbitals can bond to the equatorial chlorines (E').

c. The d_z² orbital extends farther than the p orbitals, making the axial bonds a bit longer.

13. 每一小題 2 分，共 8 分



b. The 1a₂'' orbital near the middle of the figure is the π-bonding orbital.

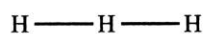
c. The LUMO, 2a₂'', is the best orbital for accepting a lone pair.

d. The 1a₂'' orbital is formed by adding all the p_z orbitals together. The 2a₂'' orbital is formed by adding the B p_z orbital and subtracting the three F p_z orbitals.

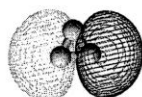
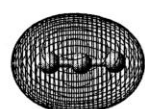
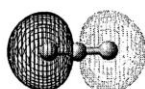
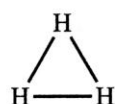
14. 配分-linear:4 分，cyclic:4 分，stable: 2 分，共 10 分

a.

Linear



Cyclic



In the linear arrangement, the molecular orbitals shown, from bottom to top, are bonding, nonbonding, and antibonding, with only the bonding orbital occupied. In the cyclic geometry, the lowest energy orbital is bonding, and the other two orbitals are degenerate, each with a node slicing through the center; again, only the lowest energy orbital is occupied.

- b. Cyclic H_3^+ is slightly more stable than linear H_3^+ , based on the energy of the lowest orbital in an AM1 calculation (-28.4 eV versus -26.7 eV).

15. 配分(a)5 分- 老師講義和課本的皆可(略)

(b) 5 分- LUMO: π acid, HOMO: σ base;

共 10 分