（102）輔仁大學碩士班招生考試題目	考試日期：102 年 3 月 8 日第 2 節
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科目：無機化學　　系所組：化學系碩士班甲組

1. (a) (1) Determine the possible values for the l and m_l quantum numbers for a $5d$ electron, a $4f$ electron, and a $7g$ electron.
(2) Determine the possible values for all four quantum numbers for a $3d$ electron.
(3) What Values of m_l are possible for f orbitals?

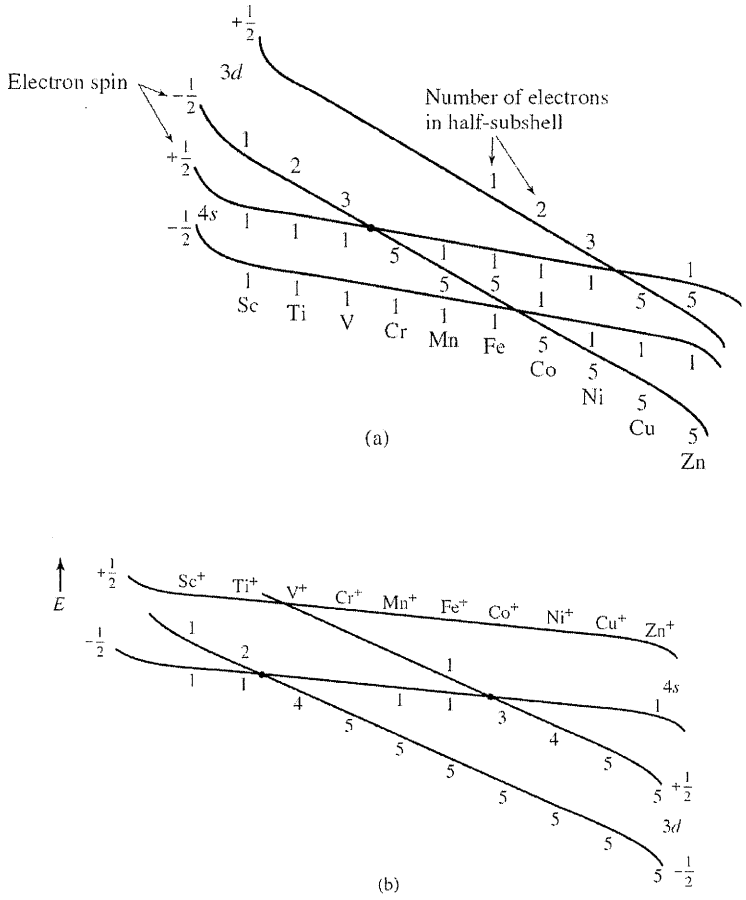
(b) Determine the Coulombic and exchange energies for the following configurations, and determine which configuration is favored (of lower energy):

(1)  and

(2) 

(c) Using the Figure 1 to explain the following phenomena:
(1) The electron configuration of Cr is $[Ar]4s^13d^5$ rather than $[Ar]4s^23d^4$.
(2) The electron configuration of Fe^+ is $[Ar]4s^13d^6$ rather than $[Ar]4s^23d^5$.

Figure 1.



(10 points)

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2. 「Slater Shielding Rule」：

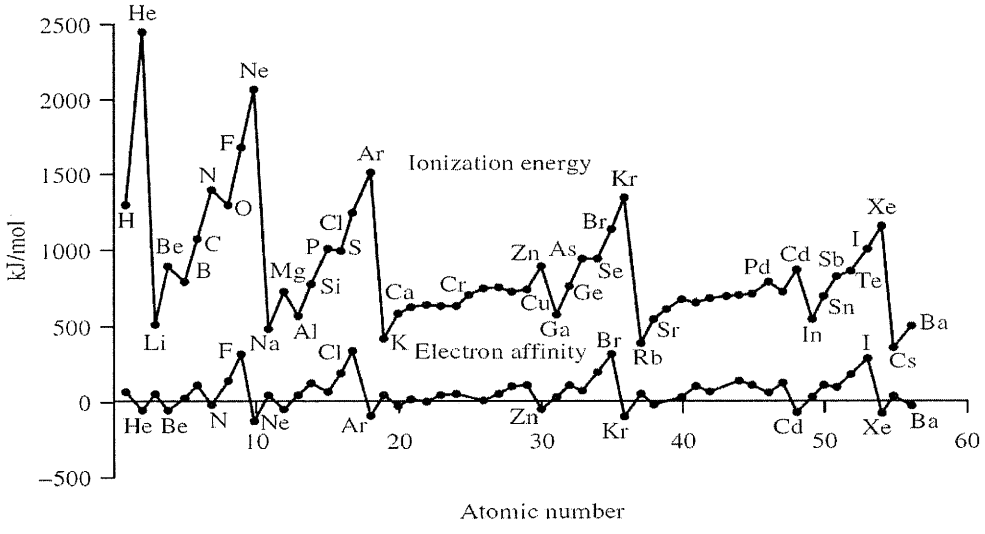
- The electrons are grouped in the following order : 1*s*; 2*s* and 2*p*; 3*s* and 3*p*; 3*d*; 4*s* and 4*p*; 4*d*; 4*f*, and so on – n*s* and n*p* electrons always being considered as a single group.
- Electrons in groups above that of a particular electron do not shield it at all.
- A shielding of 0.35 is considered by each other electron in the same group (except for a 1*s* electron, which contributes 0.30 to the shielding of the other 1*s* electron).
- For *d* and *f* electrons the shielding is 1.00 for each in the underlying groups. For *s* and *p* electrons the shielding from the immediately underlying shell (i.e., n-1) is 0.85 for each electron; the shielding from groups further in is 1.00 for each electron.

Using the Slater's rules, Figure 2, and Figure 1 to answer the following questions:

(a) For 4s and 3d electrons of Cu, which type of electron is more likely to be lost when copper forms a positive ion? Figure 1 can give you an opposite conclusion, discuss them.

(b) Use Slater's rules to calculate the effective nuclear charge Z* for the elements Li through F. How is the trend in Z* reflected in the ionization energies in this period?

Figure 2.



(10 points)

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3. IE and EA energies of elements are shown in the Table.

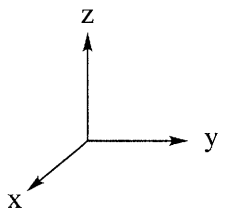
	Ionization Energy (IE, eV)	Electron Affinity (EA, eV)
H	13.598	0.7542
Na	5.139	0.548
Cl	12.967	3.617
Br	11.814	3.365

(a) Which of the following is softer ? Why?
(1) Cl or Br
(2) H or Na

(b) Which of the element is much absolute electronegativity ? Why?
(1) Cl or Br
(2) H or Na

(10 points)

4. For the molecular, O═C═C═O,



(a) Find the 3N freedom terms .
(b) Fill the following spaces of Table for the target molecule.

	terms
$\Gamma_{trans.}$	
$\Gamma_{roration}$	
$\Gamma_{vibration}$	
Γ_{IR}	
Γ_{Raman}	
$\Gamma_{Coincidence}$	
Γ_{Silent}	

(c) What the vibration terms belong to stretching mode(s)?

O═C═C═O
← →

(15 points)

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Table1. Character Table for D_{2h} and $D_{\infty h}$.

D_{2h}	E	$C_2(z)$	$C_2(y)$	$C_2(x)$	i	$\sigma(xy)$	$\sigma(xz)$	$\sigma(yz)$		
A_g	1	1	1	1	1	1	1	1		x^2, y^2, z^2
B_{1g}	1	1	−1	−1	1	1	−1	−1	R_z	xy
B_{2g}	1	−1	1	−1	1	−1	1	−1	R_y	xz
B_{3g}	1	−1	−1	1	1	−1	−1	1	R_x	yz
A_u	1	1	1	1	−1	−1	−1	−1		
B_{1u}	1	1	−1	−1	−1	−1	1	1	z	
B_{2u}	1	−1	1	−1	−1	1	−1	1	y	
B_{3u}	1	−1	−1	1	−1	1	1	−1	x	

$D_{\infty h}$	E	$2C_\infty^{\phi}$	...	$\infty\sigma_v$	i	$2S_\infty^{\phi}$	...	∞C_2		
$A_{1g} \equiv \Sigma_g^+$	1	1	...	1	1	1	...	1		$x^2 + y^2, z^2$
$A_{2g} \equiv \Sigma_g^-$	1	1	...	−1	1	1	...	−1	R_z	
$E_{1g} \equiv \Pi_g$	2	$2\cos\phi$	...	0	2	$-2\cos\phi$	...	0	(R_x, R_y)	(xz, yz)
$E_{2g} \equiv \Delta_g$	2	$2\cos 2\phi$	...	0	2	$2\cos 2\phi$	...	0		$(x^2 - y^2, xy)$
...	...	...	...	...	...	...	...	...		
$A_{1u} \equiv \Sigma_u^+$	1	1	...	1	−1	−1	...	−1	z	
$A_{2u} \equiv \Sigma_u^-$	1	1	...	−1	−1	−1	...	1		
$E_{1u} \equiv \Pi_u$	2	$2\cos\phi$	...	0	−2	$2\cos\phi$	...	0	(x, y)	
$E_{2u} \equiv \Delta_u$	2	$2\cos 2\phi$	...	0	−2	$-2\cos 2\phi$	...	0		
...	...	...	...	...	...	...	...	...		

Table 2. The relation table between D_{2h} and $D_{\infty h}$.

$D_{\infty h}$	D_{2h}
Σ_g^+	A_g
Σ_g^-	B_{1g}
Π_g	$B_{2g}+B_{3g}$
Δ_g	A_g+B_{1g}
Σ_u^+	B_{1u}
Σ_u^-	A_u
Π_u	$B_{2u}+B_{3u}$
Δ_u	A_u+B_{1u}

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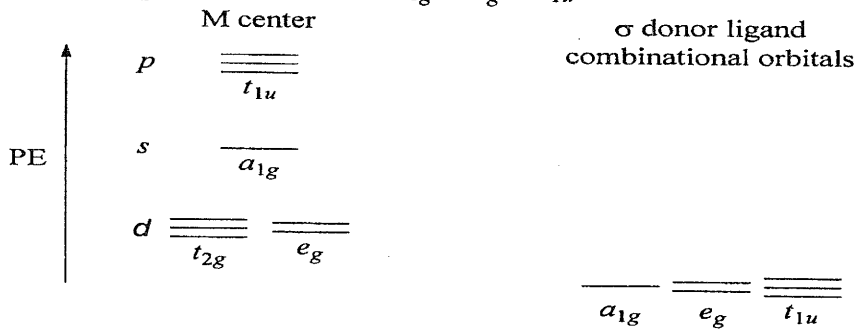
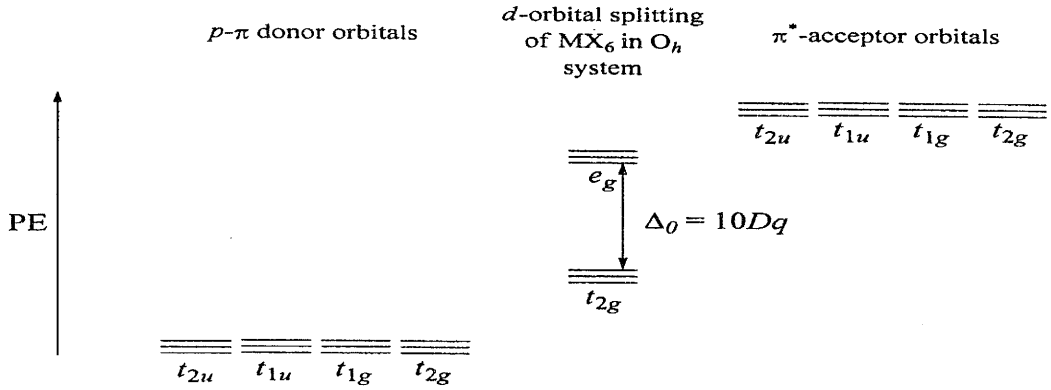
5. For the six coordinational σ-ligang metal complexes, MX_6 in O_h group, the metal center orbital represented as $t_{2g} + e_g$ (d), a_{1g} (s), and t_{1u} (p), and the six σ-donor combinational orbitals represented as the $a_{1g} + e_g + t_{1u}$:



(a) Find the Molecular Orbitals of σ-type MX_6 complexes in O_h system.

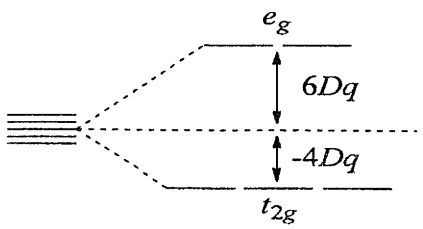
(b) Find the t_{1u} wave function of the combinational σ-donor ligand orbitals.

(c) The crystal field theory focus on the d-orbitals splitting in the MX_6 of O_h system. When p-π donor or π^* acceptor contribute to the d orbital splitting, find simple Molecular Orbitals of MX_6 in O_h system including π-orbitals contributions.



(d) When π^* acceptor orbitals or p-π donor orbitals contribute to the simple d-orbitals splitting MO in O_h system. Which π system increases the $10D_q$ energy, and which π system decreases the $10D_q$ energy.

(e) For the crystal field stabilized energy (CFSE) model.



Find the electronic configurations, unpair electron, and spin-only magnetic moment, ($\mu_s = g\sqrt{s(s+1)}$, $g = 2.00$) of d^1 to d^{10} electronic configuration ions.

(20 points.)

6. The stepwise stability constants in aqueous solution at 25°C for the formation of the ions $[M(en)(H_2O)_4]^{2+}$, $[M(en)_2(H_2O)_2]^{2+}$, and $[M(en)_3]^{2+}$ for copper and nickel are given in Table. Why is there such a difference in the third values? (Hint: Consider the special nature of d^9 complexes.) (10 points.)

	$[M(en)(H_2O)_4]^{2+}$	$[M(en)_2(H_2O)_2]^{2+}$	$[M(en)_3]^{2+}$
Cu	3×10^{10}	1×10^{9}	0.1 (estimated)
Ni	2×10^{7}	1×10^{6}	1×10^{4}

7. (a) For each of the following sets, which complex would be expected to have the highest C–O stretching frequency?

(1) $Mo(CO)_3(PCl_3)_3$ $Mo(CO)_3(PCl_2Ph)_3$ $Mo(CO)_3(PPh_3)_3$

(2) $[Ta(CO)_6]^-$ $W(CO)_6$ $[Re(CO)_6]^+$

(b) Account for the following trend in IR frequencies:

$[Cr(CN)_5(NO)]^{4-}$ $\nu(NO) = 1515\ cm^{-1}$

$[Mn(CN)_5(NO)]^{3-}$ $\nu(NO) = 1725\ cm^{-1}$

$[Fe(CN)_5(NO)]^{2-}$ $\nu(NO) = 1939\ cm^{-1}$ (10 points.)

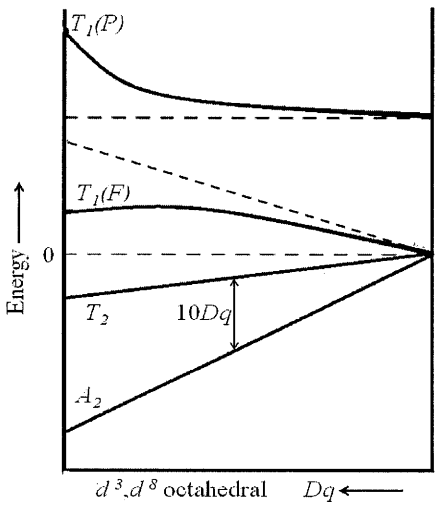
8. Based on the Orgel diagram for the d^3 and d^8 ion in an O_h system, the optical transition of spin-allowed transitions are,

$\upsilon_1 = 10Dq \equiv {}^nA_2 \rightarrow {}^nT_2$ .....(1)

$\upsilon_2 = 18Dq\text{-}c \equiv {}^nA_2 \rightarrow {}^nT_1(F)$ .....(2)

$\upsilon_3 = 15B+12Dq+c \equiv {}^nA_2 \rightarrow {}^nT_1(P)$.....(3)

where c is the energy solution of the state mixing, n is the spin multiplicity. (3pts,each)



(a) Find the spin multiplicity of "n" for d^3 and d^8 ion in an O_h system.

(b) The spin-allowed transitions of $[Ni(H_2O)_6]^{2+}$ and $[Cr(H_2O)_6]^{3+}$ showed in the Table, find the Dq,c and B values for each complex.

	$[Ni(H_2O)_6]^{2+}$	$[Cr(H_2O)_6]^{3+}$
υ_1	$8500\ cm^{-1}$	$17400\ cm^{-1}$
υ_2	$15400\ cm^{-1}$	$24600\ cm^{-1}$
υ_3	$26000\ cm^{-1}$	$37900\ cm^{-1}$

(c) The transitions energy of $[Ni(NH_3)_6]^{2+}$ are $\upsilon_1 = 10750\ cm^{-1}$, $\upsilon_2 = 17500\ cm^{-1}$, find Dq and B values with the d^8 Tanabe-Sugano Diagram. (15 points.)

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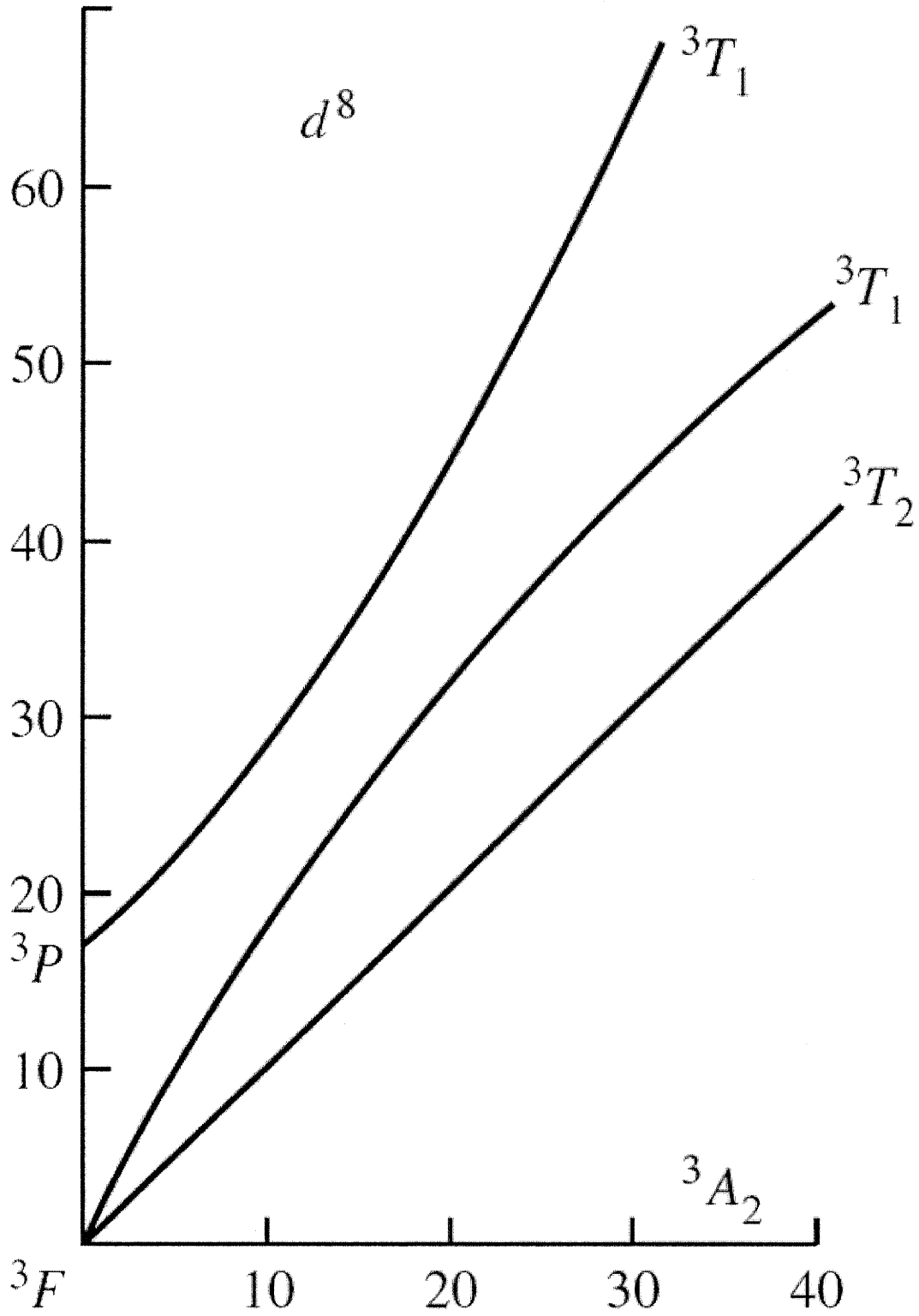

Tanabe-Sugano Diagram of d^8 ion.

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