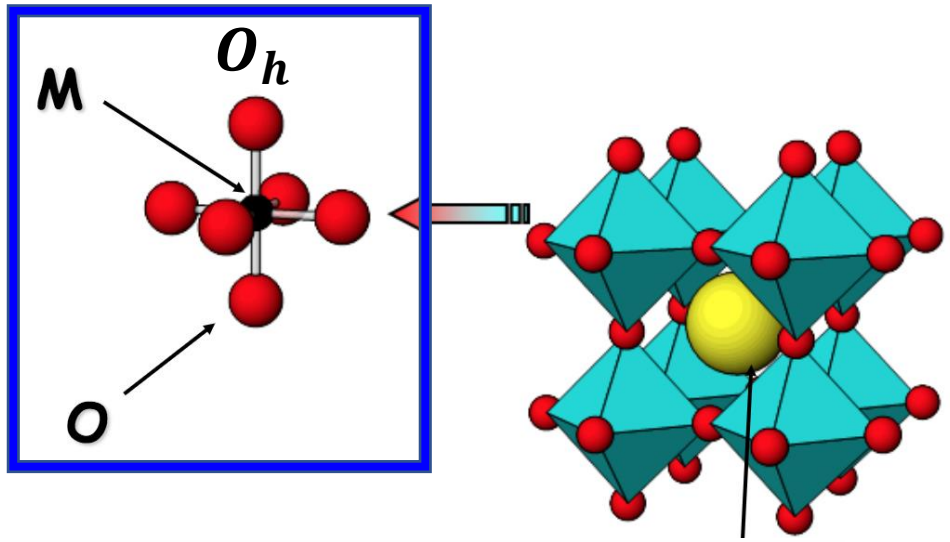
Double Exchange *IV*: *Ligand Field Effects*

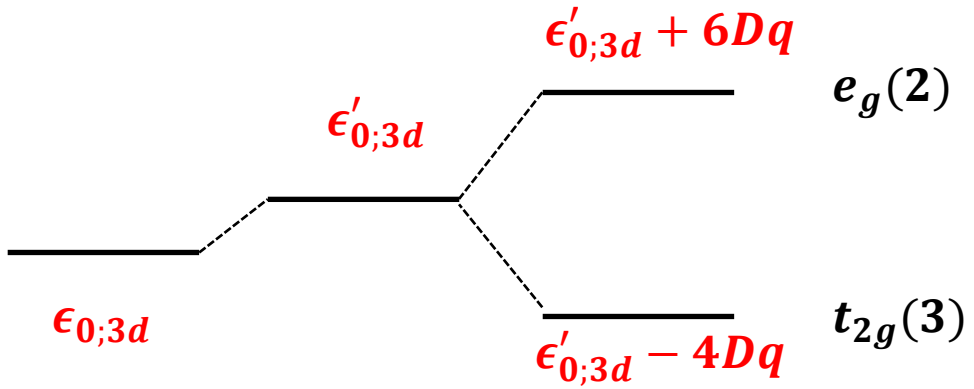
Detian Yang

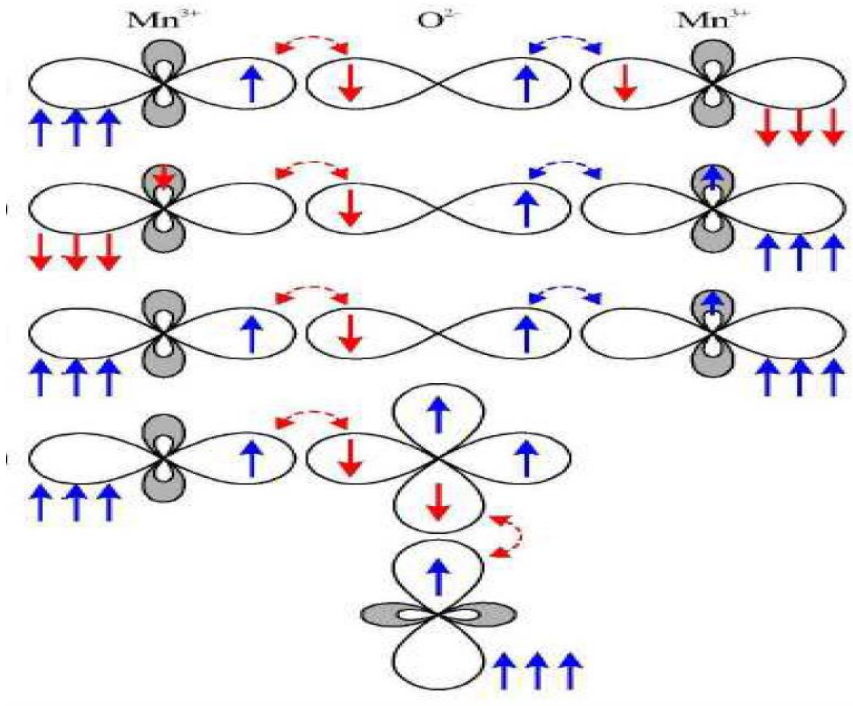
07/31/2020

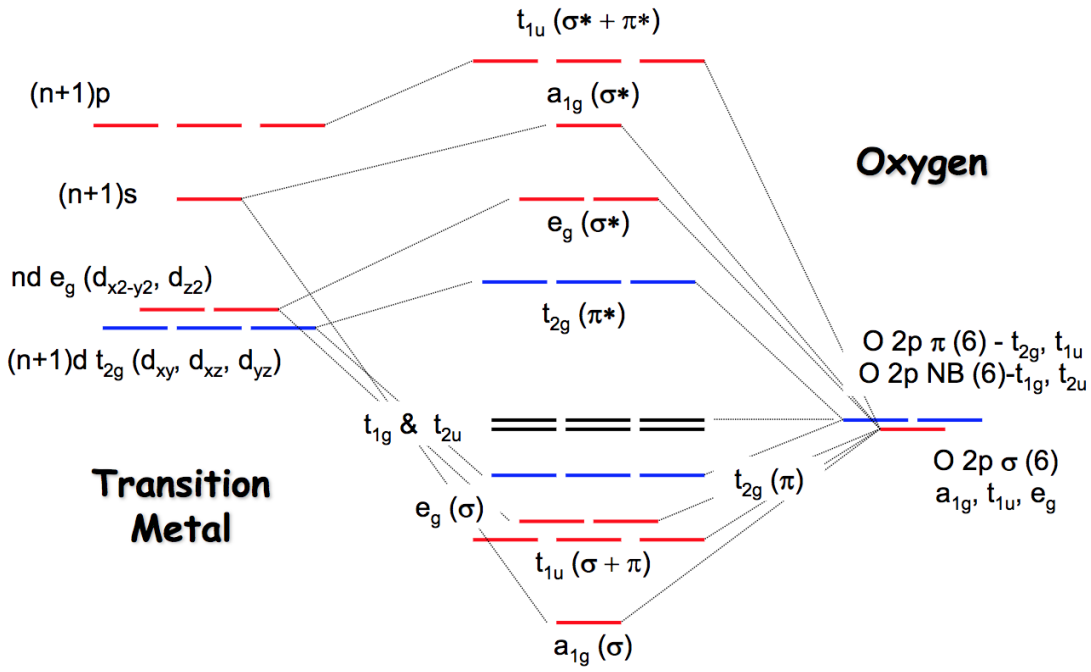
Perovskite Crystal Structure



Energy Level







Ligand-Field Theory

Part I: A Simple Introduction(07/30/2020)

Part II: Molecular-orbital theory (Covalent Bond Theory)

II.I: Theoretical Frame of Magnetism for Insulators (1 Month)

II.II: $3d^1$ Covalent Bond Method(3 Month)

II.III: Superexchange

II.IV: Goodenough- Kanamori Rule (4 Months)

Part III: Crystal Field theory (Electrostatic Theory)

III.I: $3d^1$ Model-Based Method (07/03/2020)

III.II: $3d^1$ Symmetry-Based Method (2 Months)

III.III: $3d^N, \mathrm{N} \geq 2$ Model-Based Method (5 Months)

III.IV: $3d^1$ Model-Based Method: Phillips-Cohen-Heine Theorem (6 Months)

Part I: A Simple Intro to Ligand-Field Theory

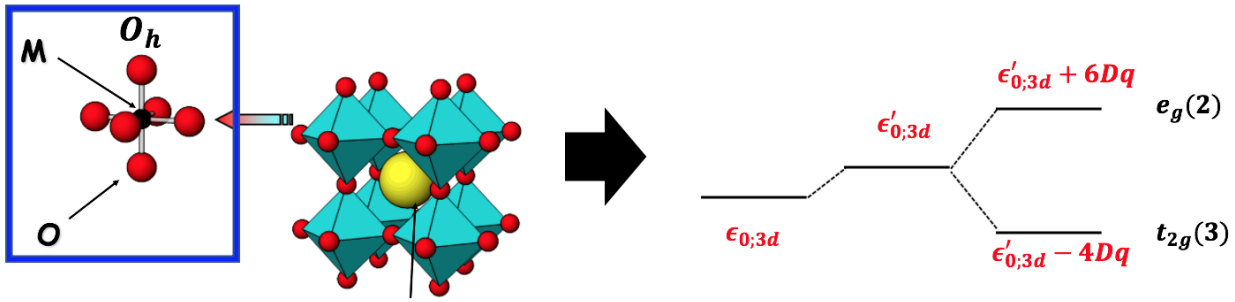
J. Griffith and L. Orgel , Q. Rev., Chem. Soc., 1957, 11 , 381 —393

What is ligand-field theory?

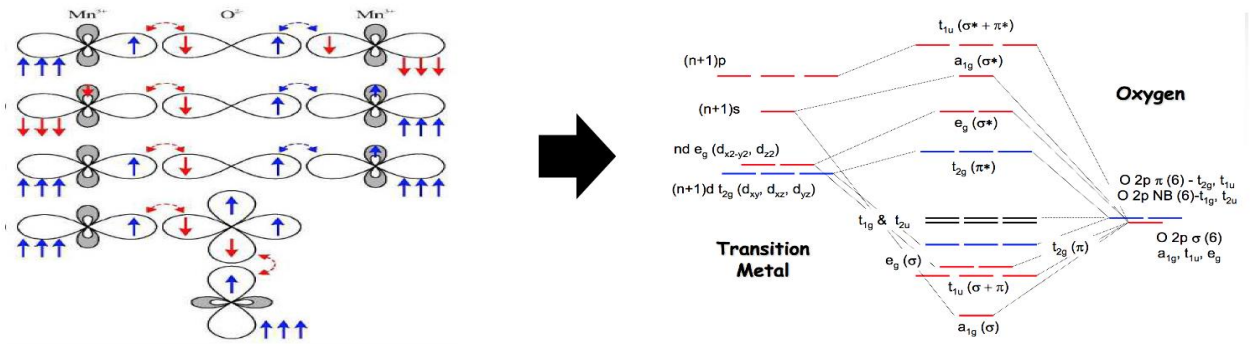
Deal with the effect of the neighbors of a centered *transition-metal magnetic ion* on the behavior of the electrons and hence the properties of the magnetic ion

Two aspects:

(1) Crystal Field Theory (Electrostatic theory)



(2) Molecular-orbital Theory(Covalent Bond Theory)



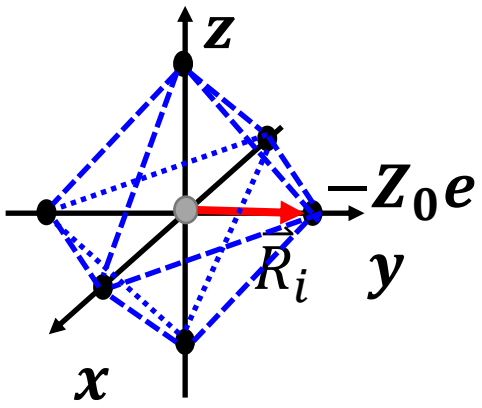
Assumptions:

1. **A combination of CFT and MOT**
2. $MX_6(O_h)$
3. **Ignore spin-orbital coupling**
4. **Ignore Phonon Modes**

H. Bethe, *Ann.* Physik, 1929, 3, 133
J. H. Van Vleck, *Phys. Review,* **1932, 41, 208.**
R . Schlapp and W. G. Penney, *Phys. Review,* **1932, 42, 666.**
O. M. Jordahl, *Phys. Review*, **1934, 45, 87.**
J. B. Howard, *J . Chern.* *Phys.,* **1935, 3, 813.**

J. H. **Van Vleck, *J . Chern.*** *Phys.,* **1935, 3, 807**

Crystal Field Effect: nd^1



Mathematica: symbolic operation

0) $(|R_i|, \theta_i, \phi_i)$

1) $q_{LM} = \sqrt{\frac{4\pi}{2L+1}} \sum_{i=1}^{n_{lig}} \frac{Z_i e^2}{|R_i|^{L+1}} Y_L^M(\theta_i, \phi_i)$

2) $V_{cf}(\vec{r}) = q_{00} + \sum_{M=-2}^{2} r^2 q_{2M} \sqrt{\frac{4\pi}{2L+1}} Y_2^{M*}(\theta, \phi)$

$+ \sum_{M=-4}^{4} r^4 q_{4M} \sqrt{\frac{4\pi}{2L+1}} Y_4^{M*}(\theta, \phi)$

3) $C_L^M(lm; l'm') \equiv \int_0^{\pi} d\theta sin\theta \int_0^{2\pi} d\phi Y_l^{m\dagger}(\theta, \phi)\, Y_{l'}^{m'}(\theta, \phi) Y_L^{M*}(\theta, \phi)$

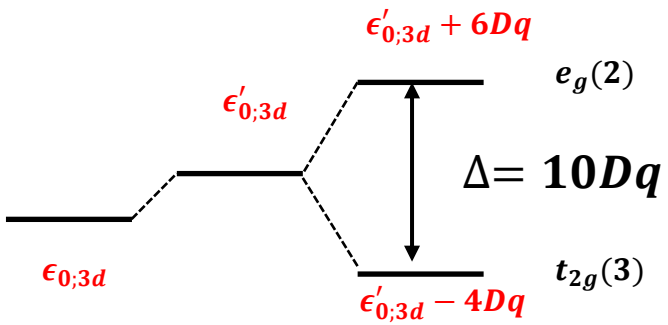
$= \sqrt{\frac{(2l+1)(2l'+1)}{4\pi(2L+1)}} \langle l\, 0\, l'\, 0 | J\, 0 \rangle \langle l\, m\, l' m' | L\, M \rangle$

4) $\langle \varphi_{0;n2m} | V_c^0 | \varphi_{0;n2m'} \rangle = \int d^3 r \varphi_{0;n2m}^{\dagger}(\vec{r})\, V_{cf}(\vec{r}) \varphi_{0;n2m'}$

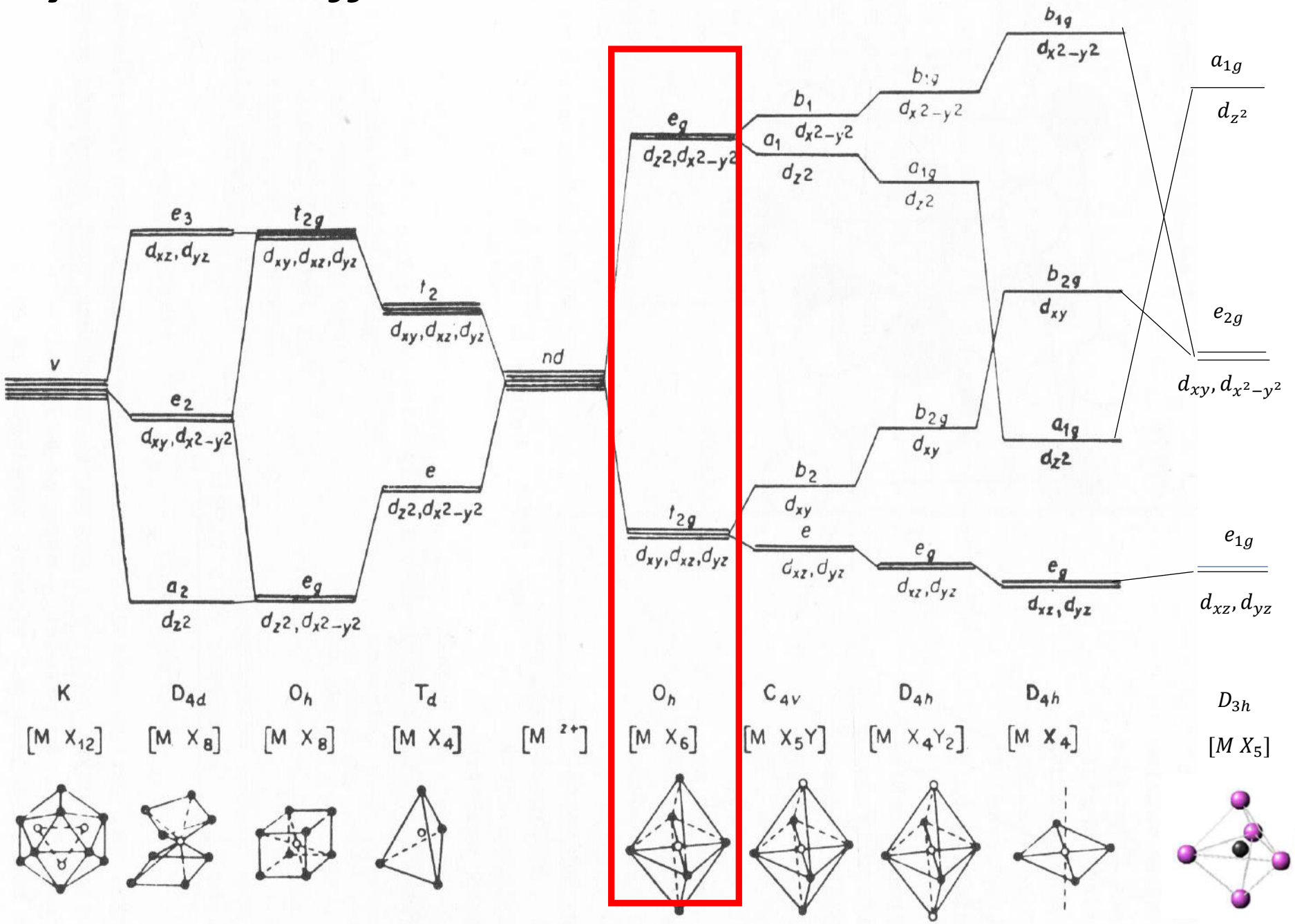
$$= \sum_{L=0}^{4} \sum_{M=-L}^{L} \sqrt{\frac{4\pi}{2L+1}} q_{LM} \int_0^{+\infty} dr\, r^{L+2} |R_{nl}(r)|^2\, C_L^M(2\, m; 2\ m')$$

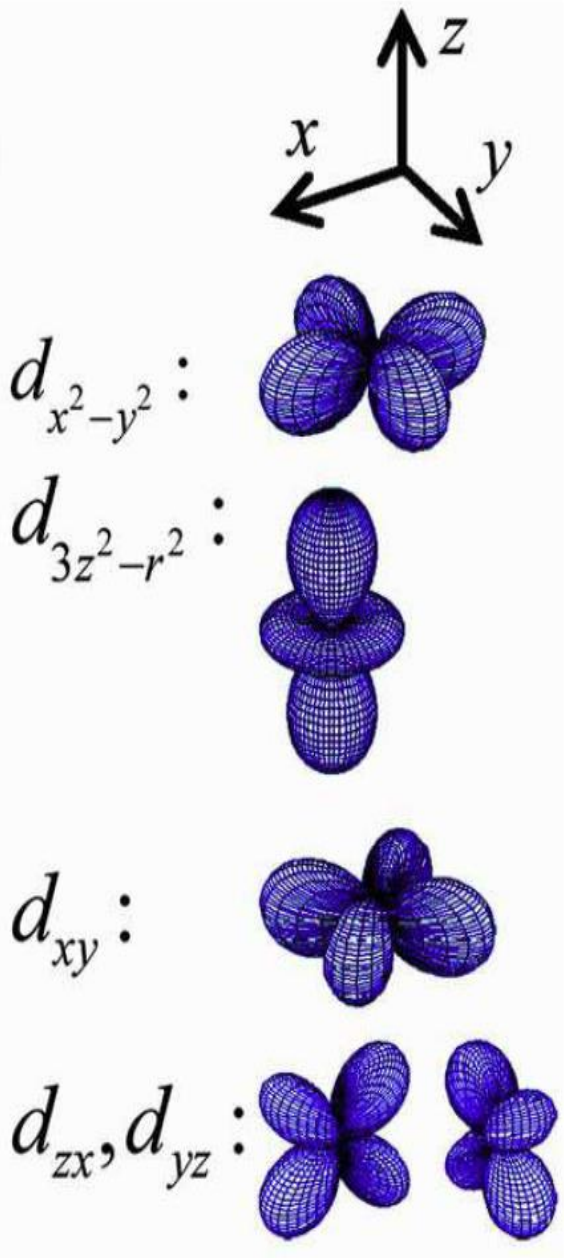
5) Diagonalize Hamiltonian

$$\begin{array}{ccccc} \varphi_{0;3d-2} & \varphi_{0;3d-1} & \varphi_{0;3d0} & \varphi_{0;3d+1} & \varphi_{0;3d+2} \end{array}$$
$$\begin{bmatrix} \langle -2|H|-2\rangle & \langle -2|V_c|-1\rangle & \langle -2|V_c|0\rangle & \langle -2|V_c|+1\rangle & \langle -2|V_c|+2\rangle \\ \langle -1|V_c|-2\rangle & \langle -1|H|-1\rangle & \langle -1|V_c|0\rangle & \langle -1|V_c|+1\rangle & \langle -1|V_c|+2\rangle \\ \langle 0|V_c|-2\rangle & \langle 0|V_c|-1\rangle & \langle 0|H|0\rangle & \langle 0|V_c|+1\rangle & \langle 0|V_c|+2\rangle \\ \langle +1|V_c|-2\rangle & \langle +1|V_c|-1\rangle & \langle +1|V_c|0\rangle & \langle +1|H|+1\rangle & \langle +1|V_c|+2\rangle \\ \langle +2|V_c|-2\rangle & \langle +2|V_c|-1\rangle & \langle +2|V_c|0\rangle & \langle +2|V_c|+1\rangle & \langle +2|H|+2\rangle \end{bmatrix}$$



Crystal Field Effect: nd^1





Crystal Field Effect: nd^1

Pros:

Up to early 1950s, $\Delta = 10Dq$ agree with experimental results as to sign and magnitude

Cons and Later Improvements:

Long-range pure Coulomb potential ✗

Kleiner(1952), Shulman and Sugano(1963): Revised potential with shielding terms

Wrong sign ✗

W. H. Kleiner, J.Chem.Phys.20, 1784(1952)

R. G. Shulman and S. Sugano, Phys. Rev. 130, 506, 517 (1963)

K. Knox, R. G. Shulman and S. Sugano, Phys. Rev. 130, 512(1963)

Tanabe and Sugano(1956), Phillips (1959), Cohen and Heine(1961): Revised d functions orthogonalized to the core functions of ligands

Better: right sign and magnitude ✓

Y. Tanabe and S. Sugano, J. Phys. Soc. Japan 11, 864 (1956)

J. C. Phillips, Phys. And Chem. Solids 11, 226 (1959)

J. C. Phillips and L. Kleinman, Phys. Rev. 116, 287(1959); 116, 880 (1959)

M. H. Cohen and V. Heine, Phys. Rev. 122, 1821 (1961)

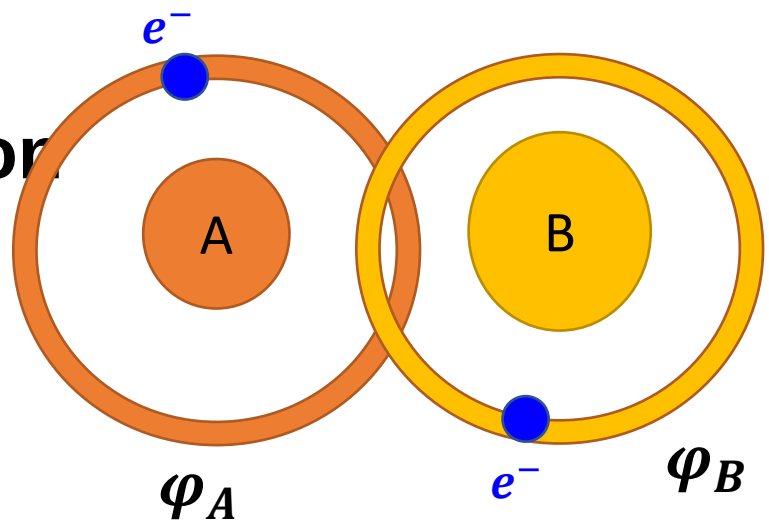
Freeman and Watson(1960): pointed out Tanabe and Sugano used wrong wavefunction and calculate the Dq with the right Hartree function

Wrong magnitude ✗

A. J. Freeman and R. E. Watson, Phys. Rev. 120, 1254(1960)

Molecular-orbital Theory

Molecular Orbital, Bond and Hybridization



MO: In molecules, a single electron moves in an averaged field of the nuclei and other electrons and its motion is described by a MO.

Hartree-Fock Method: Self-consistent Field Theory

LCAO: $|\psi\rangle = C_A|\varphi_A\rangle + C_B|\varphi_B\rangle$

Assumptions:

1. Heitler-London Method

$$\hat{H}|\psi\rangle = \epsilon|\psi\rangle \qquad \langle\varphi_A|\hat{H}|\psi\rangle = \langle\varphi_A|\epsilon|\psi\rangle \quad \langle\varphi_B|\hat{H}|\psi\rangle = \langle\varphi_B|\epsilon|\psi\rangle$$

2. NO degeneracy

3. $\epsilon_B > \epsilon_A$; $\frac{\beta}{\epsilon_B - \epsilon_A}, S \ll 1$

$$\begin{bmatrix} \epsilon_A - \epsilon & \beta - S\epsilon \\ \beta - S\epsilon & \epsilon_B - \epsilon \end{bmatrix} \begin{pmatrix} C_A \\ C_B \end{pmatrix} = 0$$

$$(\epsilon_A - \epsilon)(\epsilon_B - \epsilon) - (\beta - S\epsilon)^2 = 0$$

$$\epsilon^a \approx \epsilon_A + \frac{(\beta - S\epsilon_B)^2}{\epsilon_B - \epsilon_A} \qquad \psi^a = \frac{1}{\sqrt{N_a}}(\varphi_B - \lambda\varphi_A)$$

$$\epsilon^b \approx \epsilon_A - \frac{(\beta - S\epsilon_A)^2}{\epsilon_B - \epsilon_A} \qquad \psi^b = \frac{1}{\sqrt{N_b}}(\varphi_A + \gamma\varphi_B)$$

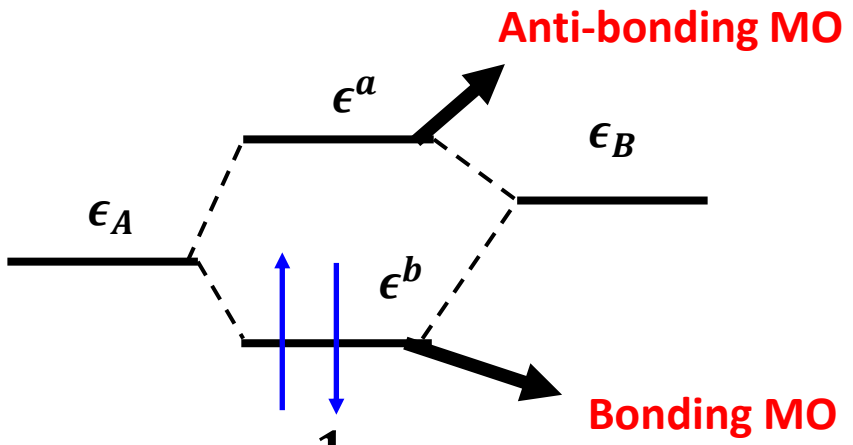
$$\epsilon_A \equiv \langle\varphi_A|\hat{H}|\varphi_A\rangle \quad \epsilon_B \equiv \langle\varphi_B|\hat{H}|\varphi_B\rangle$$

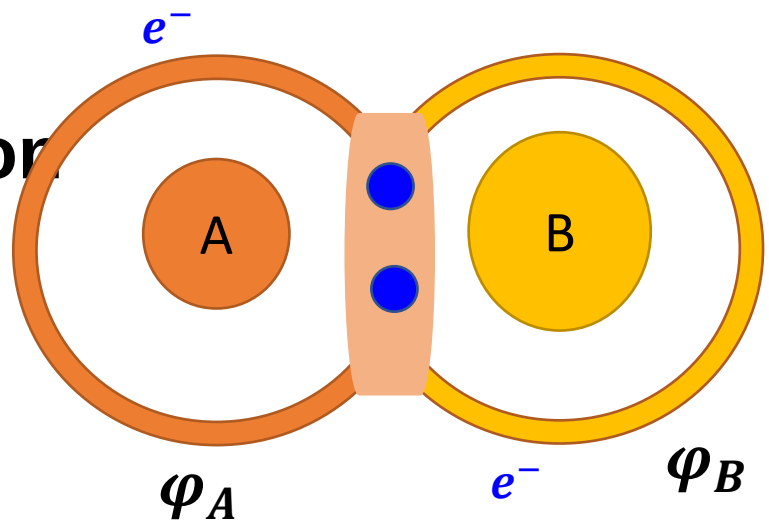
$$S \equiv \langle\varphi_A|\varphi_B\rangle \quad \beta \equiv \langle\varphi_A|\hat{H}|\varphi_B\rangle = \langle\varphi_B|\hat{H}|\varphi_A\rangle$$

Covalency Parameter $\gamma \approx -\frac{\beta - S\epsilon_A}{\epsilon_B - \epsilon_A}$ $\qquad \lambda \approx \gamma + S$

Molecular-orbital Theory

Molecular Orbital, Bond and Hybridization

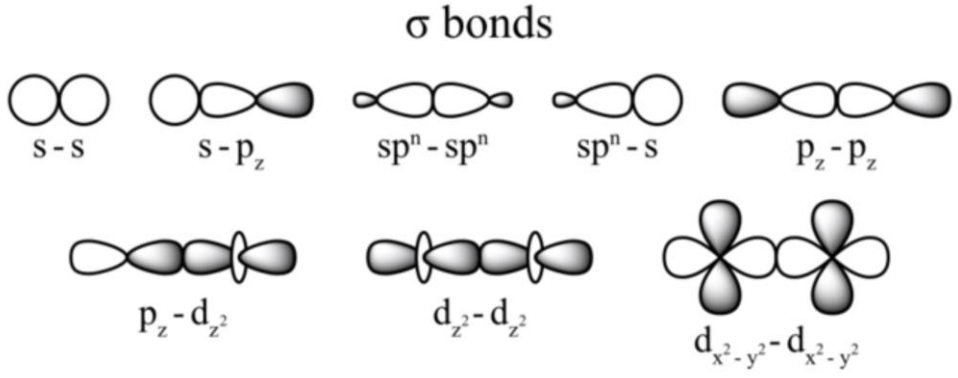


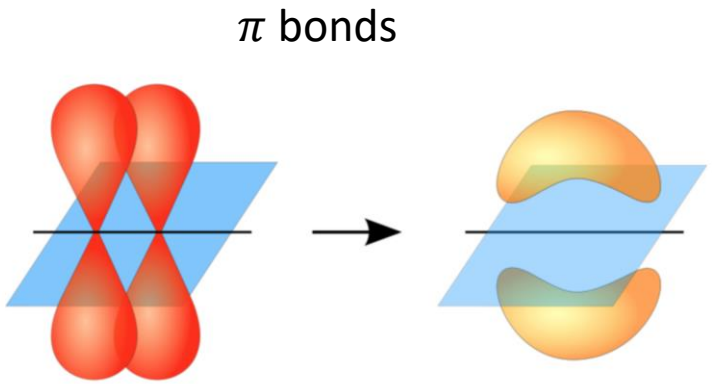


$$\chi \equiv \frac{1}{\sqrt{2}}(|\uparrow\downarrow\rangle - |\downarrow\uparrow\rangle)$$

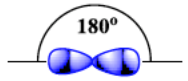
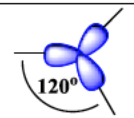
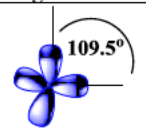
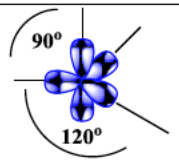
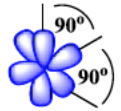
$$\Psi = \psi_1^b \psi_2^b \chi = \frac{1}{N_b}(\varphi_{1A} + \gamma\varphi_{1B})(\varphi_{2A} + \gamma\varphi_{2B})\chi$$

$$\approx \frac{1}{N_b}[\varphi_{1A}\varphi_{2A} + \gamma(\varphi_{1A}\varphi_{2B} + \varphi_{2A}\varphi_{1B})]\chi = \Psi_{ion}\chi + \gamma\Psi_{cov}\chi$$





Hybrid Orbitals and Geometry

Atomic Orbitals Used	Hybrid Orbitals Formed	Geometry	Example Compound
s,p	Two sp orbitals	 Linear	CO_2
s,p,p	Three sp^2 orbitals	 Trigonal Planar	SO_3
s,p,p,p	Four sp^3 orbitals	 Tetrahedral	$GeCl_4$
s,p,p,p,d	Five dsp^3 orbitals	 Trigonal Bipyramidal	PCl_5
s,p,p,p,d,d	Six d^2sp^3 orbitals	 Octahedral	$Mo(CO)_6$

Molecular-orbital Theory

A Naïve Bond Model of $MX_6(O_h)$: σ bond

n d electrons + 12 ligand electrons $= n + 12$

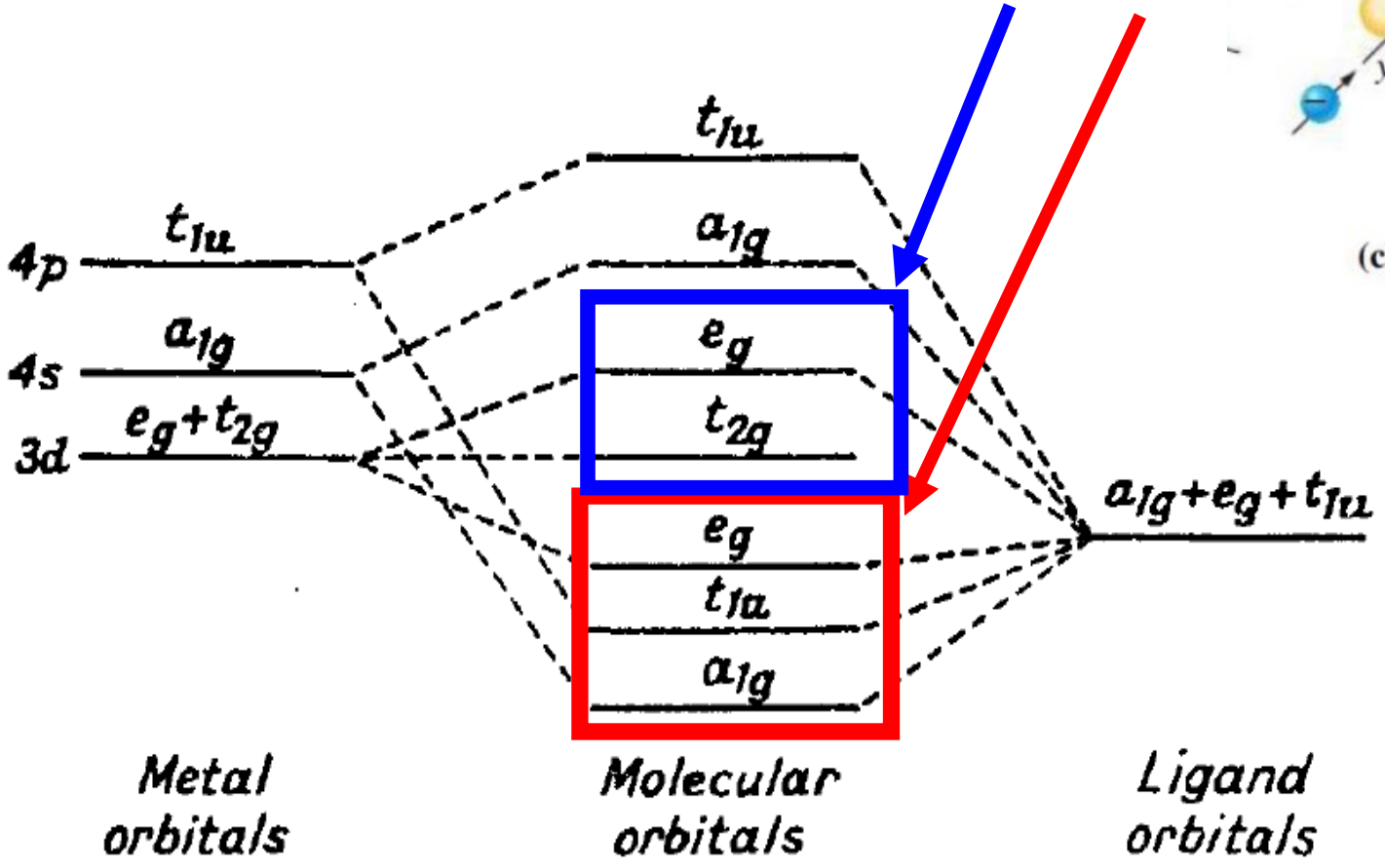
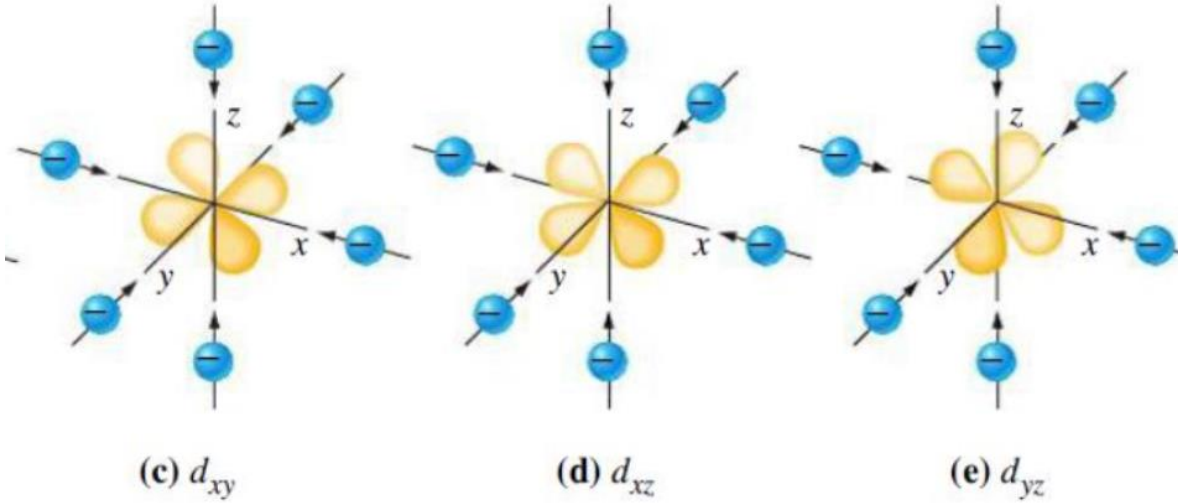
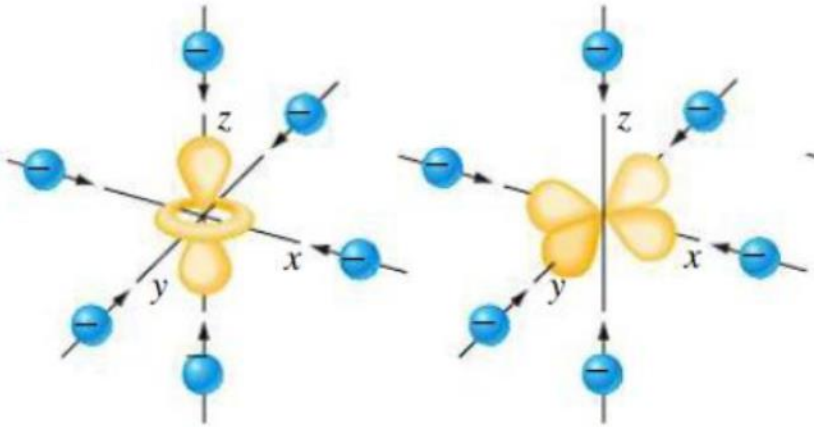


FIG. 3



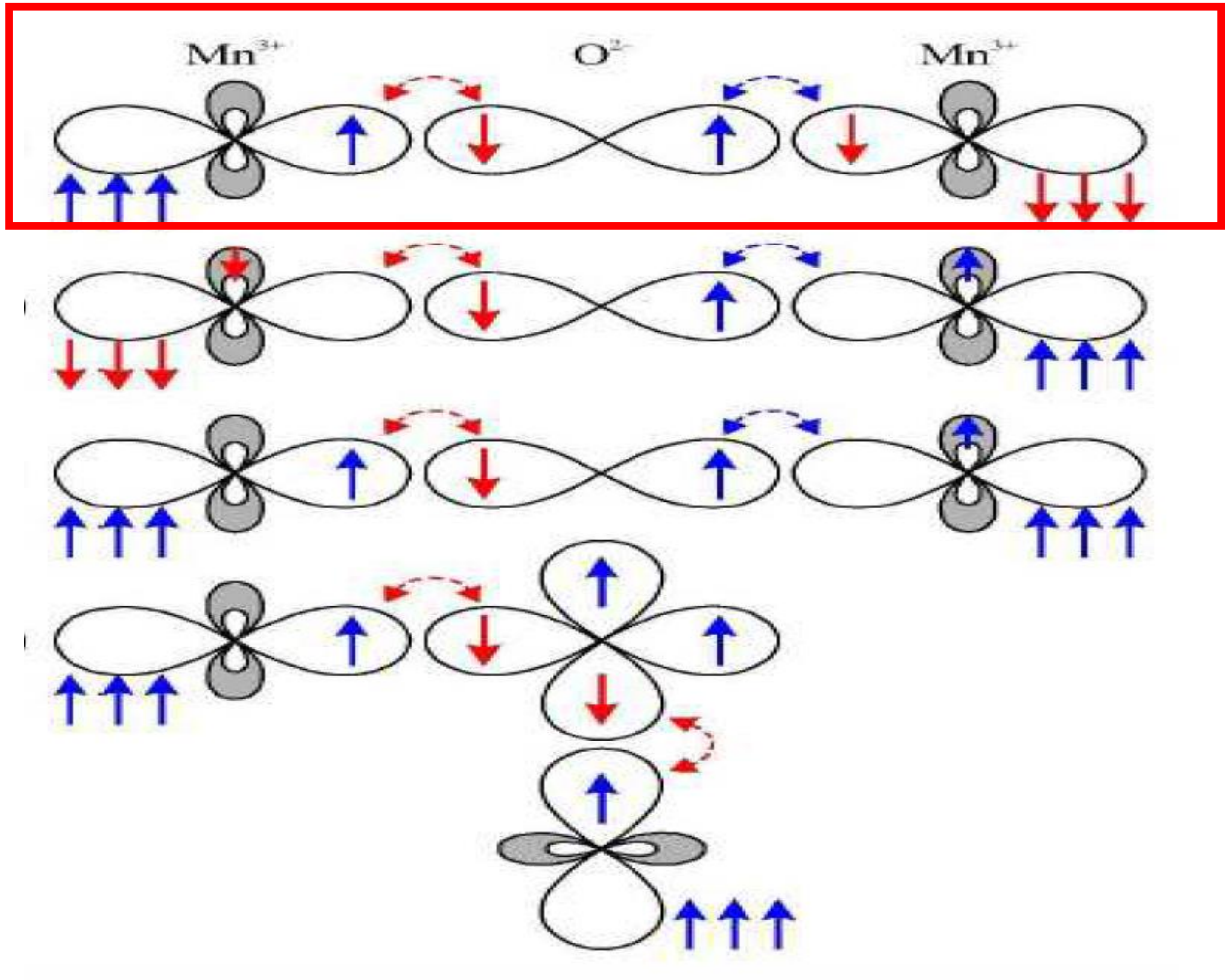
(c) d_{xy} (d) d_{xz} (e) d_{yz}



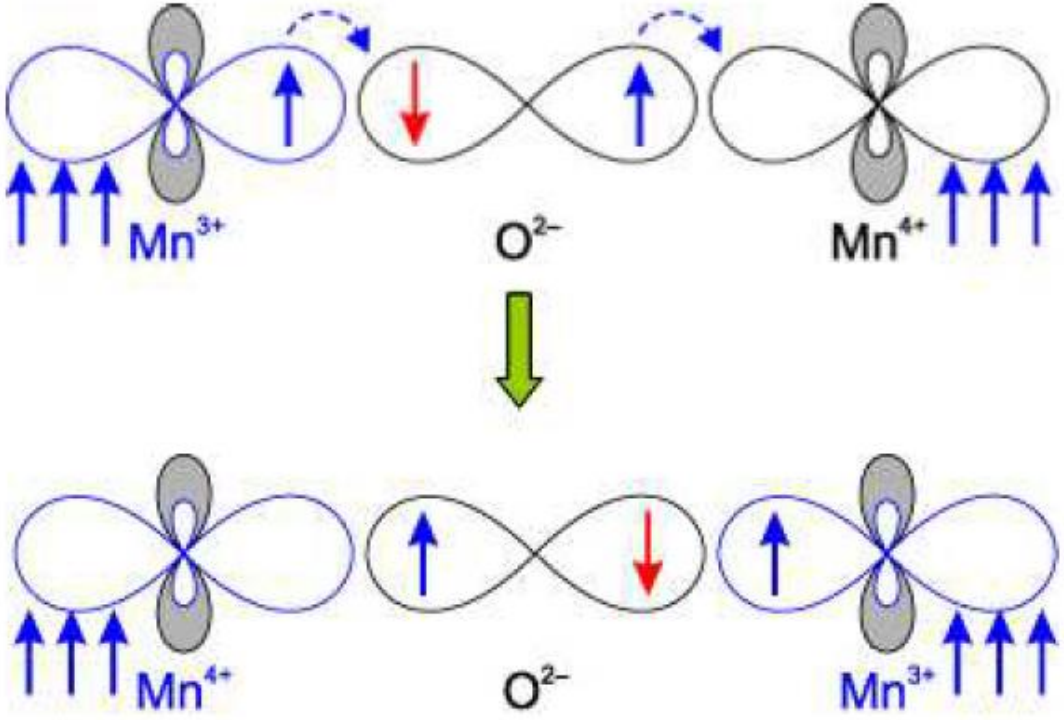
(a) d_{z^2} (b) $d_{x^2-y^2}$

Molecular-orbital Theory

Covalent Bond as the Basis of Superexchange and Double Exchange



Goodenough- Kanamori Rule: Superexchange



Double Exchange

Ground State for nd^N in Cubic Crystal Field

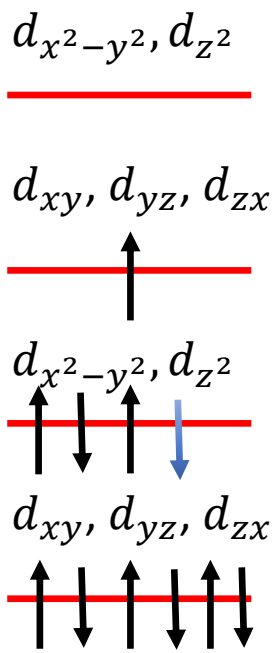
Two separate tendencies for $3d$ electrons:

(1) to occupy the orbitals of lowest energy in the ligand field

(2) to go into different orbitals with their spins parallel

$3d^1$: $[Ti(H_2O)_6]^{3+}$

$3d^9$: $[Cu(H_2O)_6]^{2+}$



$\Delta = 20400 cm^{-1}$

$\Delta = 12500 cm^{-1}$

Similarly for $3d^2, 3d^3, 3d^8$

Minimize Total Energy

Δ v.s. $\Pi = \Pi_c + \Pi_e$

L. E. Orgel, J.Chem. Phys., 1955, 23,1004.

TABLE 1. *d-Electron arrangements in octahedral complexes.*
N = Number of distinct pairs of electrons with parallel spins.

Number of d electrons	Arrangement in weak ligand field		N	Arrangement in strong ligand field		N	Gain in orbital energy in strong field
	t_{2g}	e_g		t_{2g}	e_g		
1	↑	—	0	↑	—	0	0
2	↑↑	—	1	↑↑	—	1	0
3	↑↑↑	—	3	↑↑↑	—	3	0
4	↑↑↑	↑	6	↑↓↑↑	—	3	Δ
5	↑↑↑	↑↑	10	↑↓↑↓↑	—	4	2Δ
6	↑↓↑↑	↑↑	10	↑↓↑↓↑↓	—	6	2Δ
7	↑↓↑↓↑	↑↑	11	↑↓↑↓↑↓	↑	9	Δ
8	↑↓↑↓↑↓	↑↑	13	↑↓↑↓↑↓	↑↑	13	0
9	↑↓↑↓↑↓	↑↓↑	16	↑↓↑↓↑↓	↑↓↑	16	0

Ground State for nd^N in Cubic Crystal Field

$$3d^4 - 3d^7$$

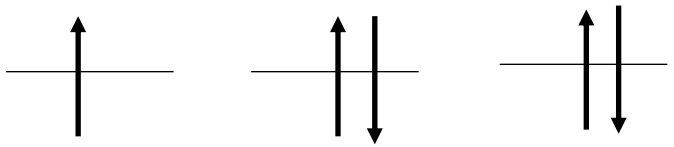
(1) putting as many as possible into the low-energy t_{2g} orbital

(2) distributing them so as to maintain a maximum number of parallel spins

Strong-field case: $3d^6$ ferrocyanides $[Fe(CN)_6]^{4-}$, $3d^5$ **Ferricyanides** $[Fe(CN)_6]^{3-}$, $3d^6$ $[Co(NH_3)_6]^{3-}$

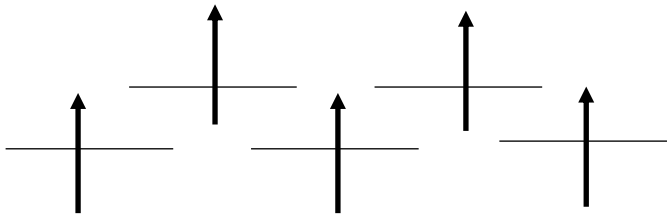
Low spin

$\Delta \gg \Pi$



Weak-field case: $3d^5$ hydrated manganous ion $[Mn(H_2O)_6]^{2+}$, $3d^5$ $[Fe(H_2O)_6]^{3+}$, $3d^6$ $[Fe(H_2O)_6]^{2+}$

High spin



$\Delta \ll \Pi$

TABLE 1. *d-Electron arrangements in octahedral complexes.*
N = Number of distinct pairs of electrons with parallel spins.

Number of d electrons	Arrangement in weak ligand field (t_{2g} / e_g)	N	Arrangement in strong ligand field (t_{2g} / e_g)	N	Gain in orbital energy in strong field
1	↑ / —	0	↑ / —	0	0
2	↑↑ / —	1	↑↑ / —	1	0
3	↑↑↑ / —	3	↑↑↑ / —	3	0
4	↑↑↑ / ↑	6	↑↓↑↑ / —	3	Δ
5	↑↑↑ / ↑↑	10	↑↓↑↓↑ / —	4	2Δ
6	↑↓↑↑ / ↑↑	10	↑↓↑↓↑↓ / —	6	2Δ
7	↑↓↑↓↑ / ↑↑	11	↑↓↑↓↑↓ / ↑	9	Δ
8	↑↓↑↓↑↓ / ↑↑	13	↑↓↑↓↑↓ / ↑↑	13	0
9	↑↓↑↓↑↓ / ↑↓↑	16	↑↓↑↓↑↓ / ↑↓↑	16	0

R. **Tsuchida,** ***Bull.*** Chem..***SOC.,Japan,***1938, **13,**388, 436, 471

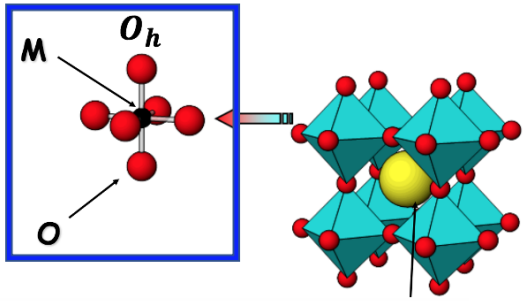
Conclusion

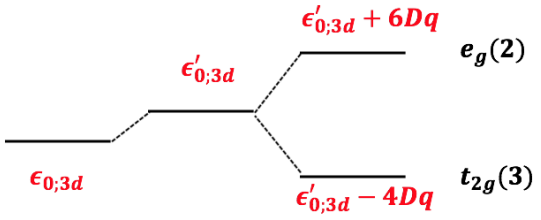
Ligand-Field Theory

Molecular-orbital theory: Orbital Overlap & Charge Transfer

Strong-field case

Weak-field case

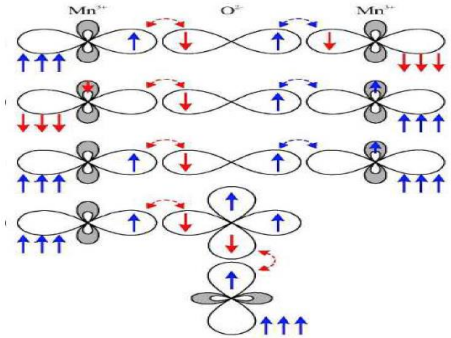


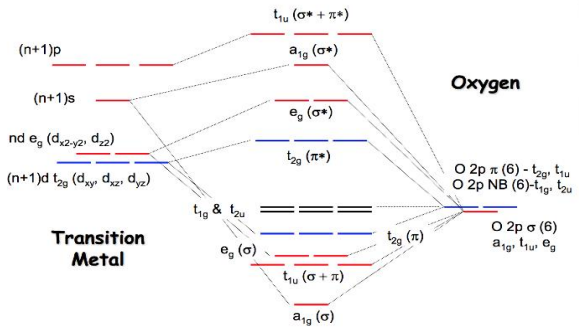


Crystal Field theory: Coulomb Interaction

Strong-field case

Weak-field case

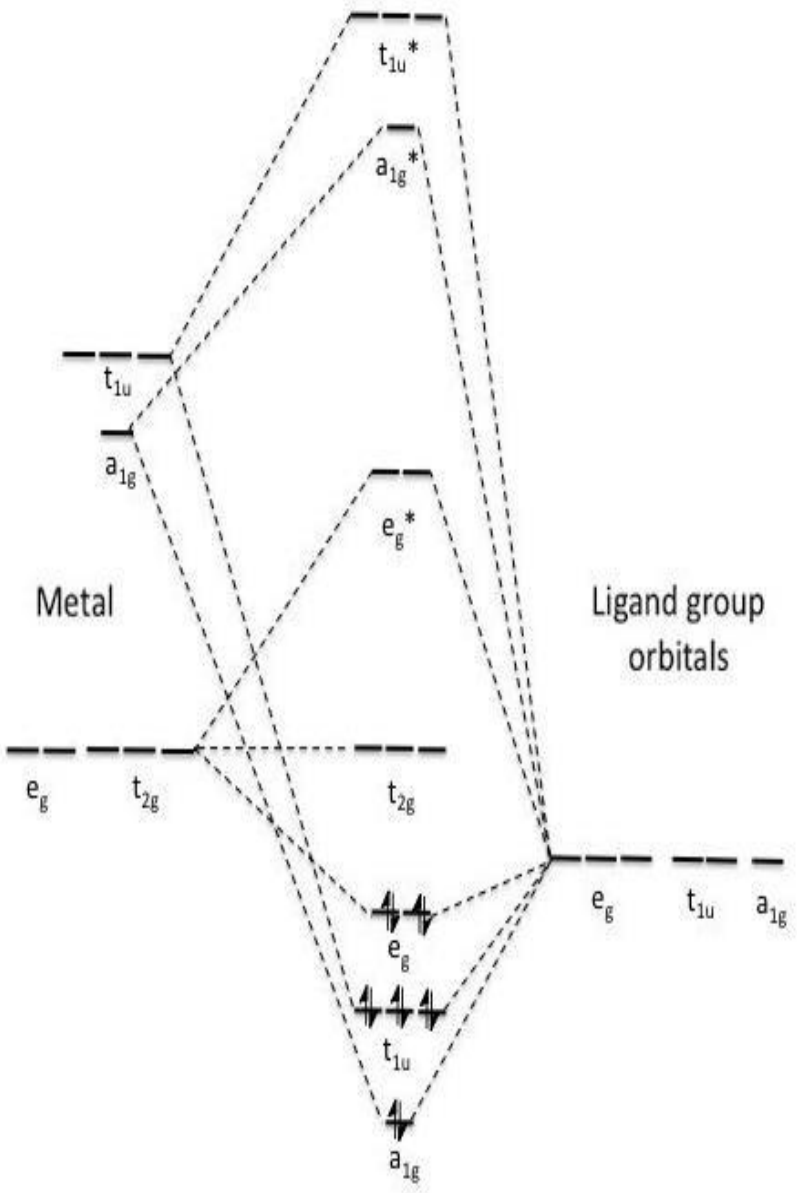




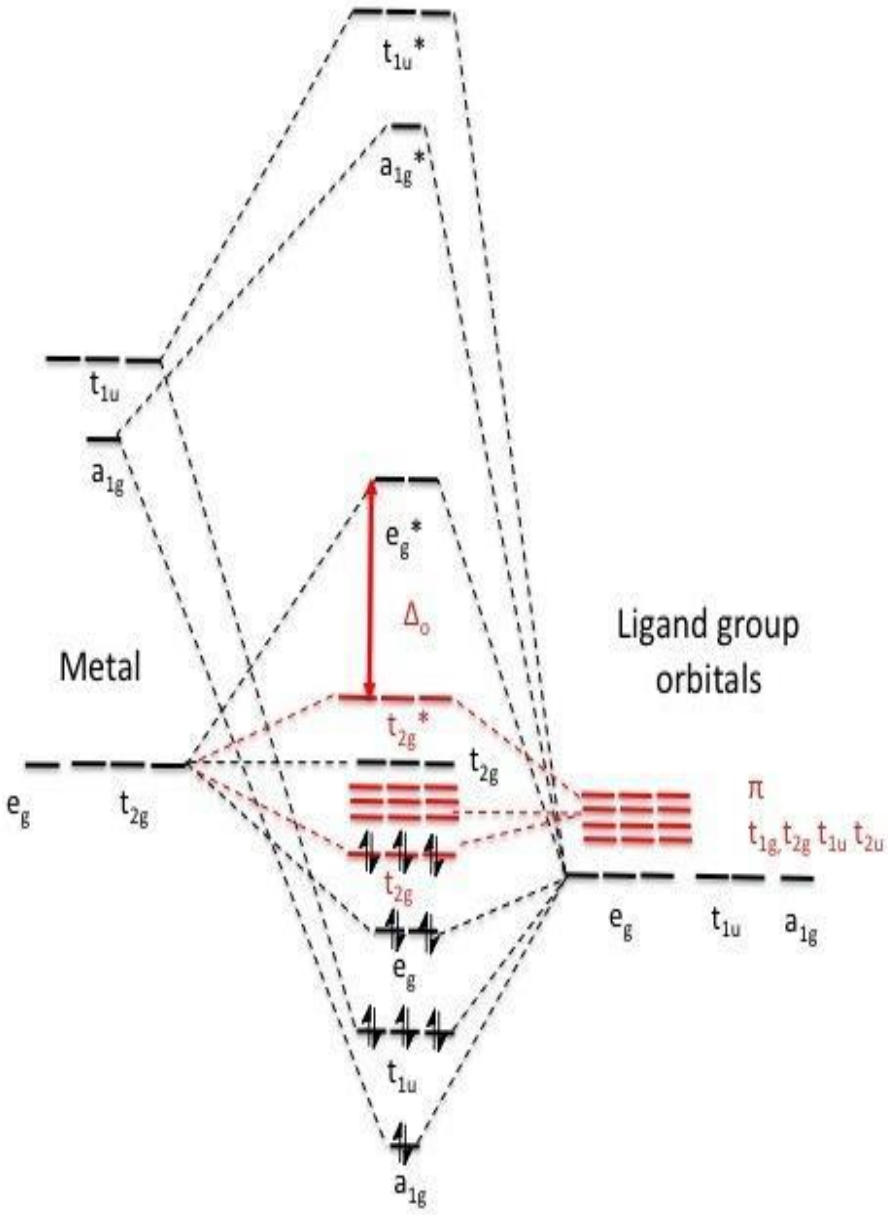
Supplementary Materials

π Bond between Transition Metal and Ligands Ion

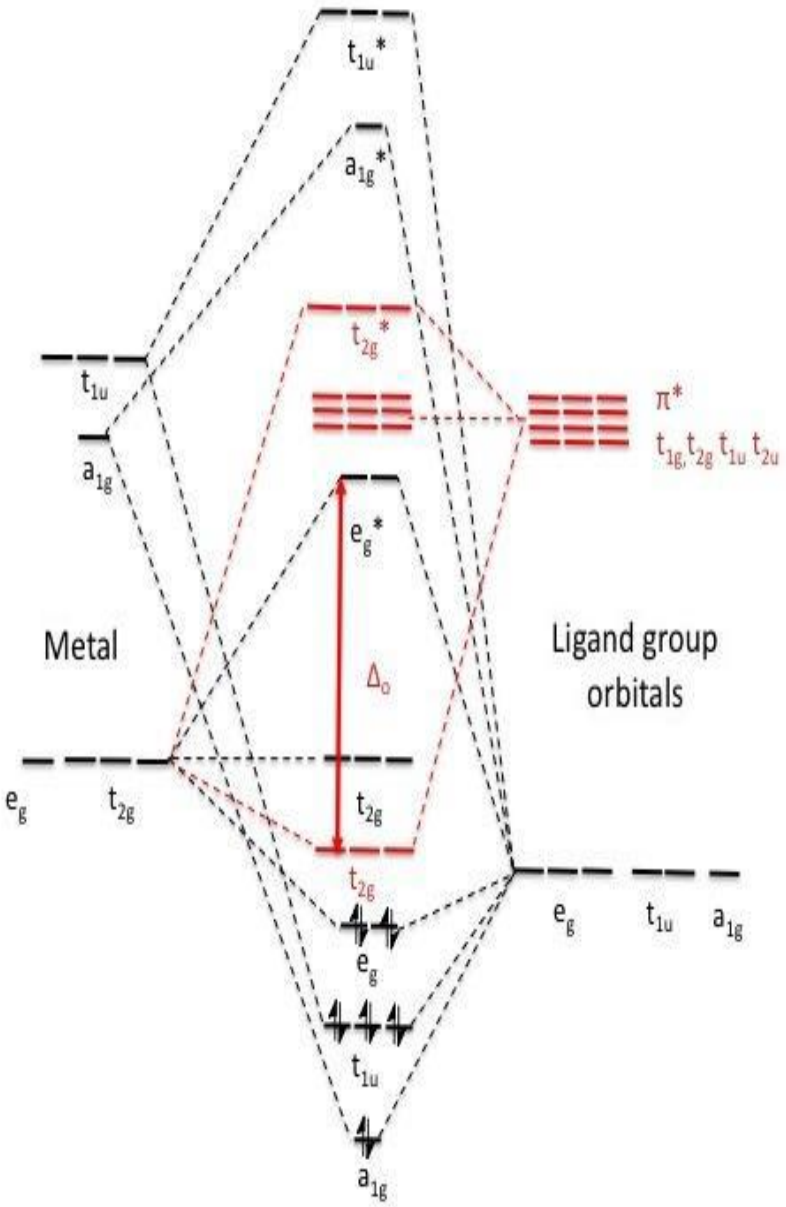
σ donor



σ donor; π donor



σ donor; π acceptor



Factors Affecting Crystal Field Splitting

Factors that Affect Crystal Field Splitting

1) Nature of the ligand:

Spectrochemical Series

$I^- < Br^- < S^{2-} < \underline{S}CN^- < Cl^- < N\underline{O}_2^- < N^{3-} < F^- < OH^- < C_2O_4^{2-} < O^{2-} < H_2O$
$< \underline{N}CS^- < CH_3C{\equiv}N < py < NH_3 < en < bpy < phen < \underline{N}O_2^- < PPh_3 < \underline{C}N^- < CO$

weak field ligands $\xrightarrow{\text{increasing } \Delta_o}$ strong field ligands

- Ligands with the same donor atoms are close together in the series.

- Ligands up to H_2O are weak-field ligands and tend to result in high-spin complexes.

- Ligands beyond H_2O are strong-field ligands and tend to result in low-spin complexes.

- CFT can not explain why certain anionic ligands lies lower in the series than neutral ligands, although reverse should be expected based on electrostatic interactions.

- It also can not explain why OH^- lies lower in the series than H_2O and NH_3, although reverse should be expected, since dipole moment of OH^- is greater than H_2O and NH_3.

Factors that Affect Crystal Field Splitting

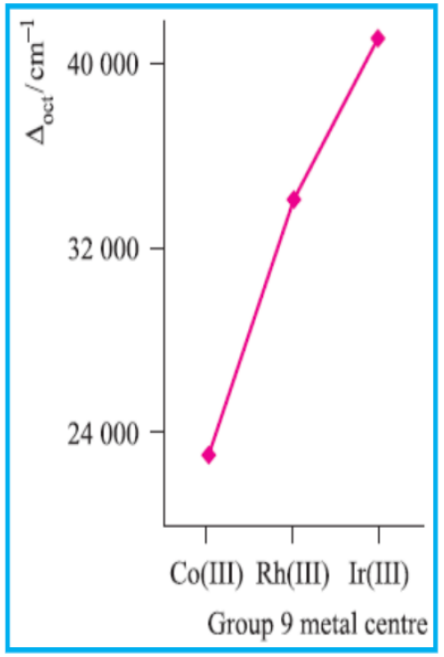
Nature of Ligand

Complex	Δ_o (cm^{-1})
$[CrCl_6]^{3-}$	13640
$[Cr(H_2O)_6]^{3+}$	17830
$[Cr(NH_3)_6]^{3+}$	21680
$[Cr(CN)_6]^{3-}$	26280

Oxidation State of Metal Ion

Complex	Δ_o (cm^{-1})
$[Fe(H_2O)_6]^{2+}$	9400
$[Fe(H_2O)_6]^{3+}$	13700
$[Co(H_2O)_6]^{2+}$	9300
$[Co(H_2O)_6]^{3+}$	18200

Nature of Metal Ion



Complex	Δ_o (cm^{-1})
$[Co(NH_3)_6]^{3+}$	24800
$[Rh(NH_3)_6]^{3+}$	34000
$[Ir(NH_3)_6]^{3+}$	41000

Thumbs of rules for the first transition series $Sc - Zn$:

A. For hydrated bivalent ions, $\Delta \in [7500 - 12500]\ cm^{-1}$

B. For hydrated tervalent ions, $\Delta \in [13500 - 21000]\ cm^{-1}$

C. Δ for their complexes with any given metal increases along the sequence: $I^-, Br^-, Cl^-, F^-, H_2O$, oxalate, pyridine, NH_3, ethylenediamine, $NO_2{}^-$, CN^-.

D. For the compounds of the second and third series is $40 - 80\%$ larger than for corresponding compounds of the first series.

Factors that Affect Crystal Field Splitting

$Mn^{2+} < Ni^{2+} < Co^{2+} < Fe^{2+} < V^{2+} < Fe^{3+} < Co^{3+} < Mn^{4+} < Mo^{3+} < Rh^{3+} < Ru^{3+} < Pd^{4+} < Ir^{3+} < Pt^{4+}$

increasing Δ_o $\longrightarrow$

- This trend is independent of ligand.

2) Oxidation State of Metal Ion: Δ_o increases with increasing oxidation number of the metal. This is due to the smaller size of the more highly charged ion, resulting in smaller metal to ligand distances and hence, a greater ligand field.

3) Nature of Metal Ion: Within any periodic group, Δ_o increases down a group (3d < 4d < 5d). This is due to the larger size of the 4d or 5d orbitals compared with the compact 3d orbitals and the consequent stronger interactions with the ligands.

- For a given ligand and a given oxidation state, Δ_o varies irregularly across the first row transition metal elements.

Complex	Δ_o (cm^{-1})
$[Cr(H_2O)_6]^{3+}$	17400
$[Fe(H_2O)_6]^{3+}$	14000
$[Co(H_2O)_6]^{3+}$	20760

Hartree-Fock Molecular Orbital Theory

Hartree-Fock Molecular Orbital Theory: A Variational Mean Field Method

Variational Method to Calculate Ground State and Energy

Energy Functional $\varepsilon[\Psi] = \dfrac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle}$

1) $\varepsilon \geq E_0, E_0$ the ground state of Hamiltonian $\hat{H}$

2) $\varepsilon = E_0$, iff Ψ is the ground state

Proof: **Spectral Theorem:** $\hat{H} = \int dE|E\rangle E\langle E|$ $\quad \hat{I} = \int dE|E\rangle\langle E|$ $\quad \hat{H}|E\rangle = E|E\rangle \quad E \geq E_0$

$$\varepsilon[\Psi] = \frac{\langle\Psi|\hat{H}|\Psi\rangle}{\langle\Psi|\Psi\rangle} = \frac{\int dE E|\langle\Psi|E\rangle|^2}{\langle\Psi|\Psi\rangle} \geq \frac{\int dE E_0|\langle\Psi|E\rangle|^2}{\langle\Psi|\Psi\rangle} = \frac{E_0\int dE|\langle\Psi|E\rangle|^2}{\langle\Psi|\Psi\rangle}$$

$$= \frac{E_0\langle\Psi|\hat{I}|\Psi\rangle}{\langle\Psi|\Psi\rangle} = E_0; \quad \text{iff } |\Psi\rangle = |E_0\rangle, \varepsilon[\Psi] = E_0$$

$$\frac{\delta\varepsilon[\Psi]}{\delta\Psi} = 0, \frac{\delta^2\varepsilon[\Psi]}{\delta\Psi^2} > 0 \quad \Rightarrow \quad |\Psi\rangle \approx |E_0\rangle$$

Hartree-Fock Molecular Orbital Theory: A Variational Mean Field Method

Variational Problem: $Hartree$-Fock Equation

With respect to the changes in the orbitals $\boldsymbol{\psi_i} \rightarrow \boldsymbol{\psi_i} + \boldsymbol{\delta\psi_i}$

Minimize $$E_{HP}[\Psi] = \langle \Psi | \hat{H}_e | \Psi \rangle = E_e[\{\boldsymbol{\psi_i}\}]$$

Lagrange Multipliers Method

$$\mathcal{L}[\{\boldsymbol{\psi_i}\}] \equiv E_e[\{\boldsymbol{\psi_i}\}] - \boxed{\sum_{i,j} \boldsymbol{\epsilon_{ij}} \left(\langle \boldsymbol{\psi_i} | \boldsymbol{\psi_j} \rangle - \boldsymbol{\delta_{ij}} \right)}$$

Keep ψ_i orthonormal

$$\frac{\delta \mathcal{L}[\{\boldsymbol{\psi_i}\}]}{\delta \boldsymbol{\psi_i}^{\dagger}} = 0 \quad \Rightarrow \quad \textbf{Hartree-Fock Equation}$$

"Self-consistent Field Theory"

$$\boldsymbol{h_i \psi_i(r_i, \sigma_i)} + \left[\sum_j^{N_e} \int \boldsymbol{dr_j\, v_{ij} |\psi_j(r_j, \sigma_j)|^2} \right] \boldsymbol{\psi_i(r_i, \sigma_i)} - \sum_j^{N_e} \int \boldsymbol{dr_j\, \psi_j^{\dagger}(r_j, \sigma_j) \psi_i(r_j, \sigma_j) v_{ij} \psi_j(r_i, \sigma_i)} = \boldsymbol{\epsilon_i \psi_i(r_i, \sigma_i)}$$

Hartree-Fock Molecular Orbital Theory: A Variational Mean Field Method

Variational Problem: Variational Calculation

$$E_e[\{\psi_i\}] \equiv \langle \Psi | \hat{H}_e | \Psi \rangle$$

$$T_e(r) \equiv \sum_{i=1}^{N_e} \frac{p_i^2}{2m_i}$$

$$H_e(r,R) \equiv [T_e(r) + V_{eN}(r,R)] + V_{ee}(r) = \sum_{i=1}^{N_e} h_i + \sum_{i>j}^{N_e} v_{ij}$$

$$V_{eN}(r,R) \equiv -\sum_{I,i}^{N,N_e} \frac{Z_I e^2}{|R_I - r_i|}$$

$$h_i \equiv \frac{p_i^2}{2m_i} - \sum_{I}^{N} \frac{Z_I e^2}{|R_I - r_i|} \quad v_{ij} \equiv \frac{e^2}{|r_i - r_j|}$$

$$V_{ee}(r) \equiv \frac{1}{2}\sum_{i,j}^{N_e} \frac{e^2}{|r_i - r_j|} = \sum_{i>j}^{N_e} \frac{e^2}{|r_i - r_j|}$$

$$\Psi(r,\sigma) = \frac{1}{\sqrt{N_e!}} \begin{bmatrix} \psi_1(r_1,\sigma_1) & \psi_2(r_1,\sigma_1) & \cdots & \psi_{N_e}(r_1,\sigma_1) \\ \psi_1(r_2,\sigma_2) & \psi_2(r_2,\sigma_2) & \cdots & \psi_{N_e}(r_2,\sigma_2) \\ \vdots & \vdots & \ddots & \vdots \\ \psi_1(r_{N_e},\sigma_{N_e}) & \psi_2(r_{N_e},\sigma_{N_e}) & \cdots & \psi_{N_e}(r_{N_e},\sigma_{N_e}) \end{bmatrix} = \frac{1}{\sqrt{N_e!}} \epsilon_{i_1 i_2 \ldots i_{N_e}} \psi_{i_1}(r_1,\sigma_1)\psi_{i_2}(r_2,\sigma_2) \ldots \psi_{i_{N_e}}(r_{N_e},\sigma_{N_e})$$

Repeated indices summed up

Completely Antisymmetric Tensor $\epsilon_{i_1 i_2 \ldots i_{N_e}} = \begin{cases} 1, & i_1 i_2 \ldots i_{N_e} \text{ is an even permutation of } 1\ 2\ 3\ \ldots N_e \\ -1, & i_1 i_2 \ldots i_{N_e} \text{ is an odd permutation of } 1\ 2\ 3\ \ldots N_e \\ 0, & \text{otherwise} \end{cases}$

Hartree-Fock Molecular Orbital Theory: A Variational Mean Field Method

Variational Problem: Variational Calculation

$$E_e[\{\psi_i\}] \equiv \langle \Psi | \hat{H}_e | \Psi \rangle = \left\langle \Psi \middle| \sum_{i=1}^{N_e} h_i + \sum_{i>j}^{N_e} v_{ij} \middle| \Psi \right\rangle = \sum_{i=1}^{N_e} \langle \Psi | h_i | \Psi \rangle + \sum_{i>j}^{N_e} \langle \Psi | v_{ij} | \Psi \rangle$$

$$\langle \Psi | h_k | \Psi \rangle = \int dr_1 dr_2 \dots dr_{N_e} \frac{1}{N_e!} \epsilon_{i_1 i_2 \dots i_{N_e}} \psi_{i_1}^\dagger(r_1, \sigma_1) \psi_{i_2}^\dagger(r_2, \sigma_2) \dots \psi_{i_{N_e}}^\dagger(r_{N_e}, \sigma_{N_e}) h_k \epsilon_{j_1 j_2 \dots j_{N_e}} \psi_{j_1}(r_1, \sigma_1)\, \psi_{j_2}(r_2, \sigma_2)$$

$$\dots \psi_{j_{N_e}}(r_{N_e}, \sigma_{N_e}) = \frac{1}{N_e!} \epsilon_{i_1 i_2 \dots i_{N_e}} \epsilon_{j_1 j_2 \dots j_{N_e}} \left[\int dr_1\, \psi_{i_1}^\dagger(r_1, \sigma_1) \psi_{j_1}(r_1, \sigma_1) \right] \dots \left[\int dr_k\, \psi_{i_k}^\dagger(r_k, \sigma_k) h_k \psi_{j_k}(r_k, \sigma_k) \right] \dots$$

$$\left[\int dr_{N_e}\, \psi_{i_{N_e}}^\dagger(r_{N_e}, \sigma_{N_e}) \psi_{j_{N_e}}(r_{N_e}, \sigma_{N_e}) \right] = \frac{1}{N_e!} \epsilon_{i_1 i_2 \dots i_{N_e}} \epsilon_{j_1 j_2 \dots j_{N_e}} \langle \psi_{i_1} | \psi_{j_1} \rangle \dots \langle \psi_{i_k} | h_k | \psi_{j_k} \rangle \dots \left\langle \psi_{i_{N_e}} \middle| \psi_{j_{N_e}} \right\rangle$$

$$= \frac{1}{N_e!} \epsilon_{i_1 i_2 \dots i_{N_e}} \epsilon_{j_1 j_2 \dots j_{N_e}} \delta_{i_1 j_1} \dots \langle \psi_{i_k} | h_k | \psi_{j_k} \rangle \dots \delta_{i_{N_e} j_{N_e}} = \frac{1}{N_e!} \epsilon_{i_1 \dots i_k \dots i_{N_e}} \epsilon_{i_1 \dots j_k \dots i_{N_e}} \langle \psi_{i_k} | h_k | \psi_{j_k} \rangle$$

$$= \sum_{i_k, j_k = 1}^{N_e} (N_e - 1)!\ \delta_{i_k j_k} \langle \psi_{i_k} | h_k | \psi_{j_k} \rangle = \sum_{i_k}^{N_e} \frac{1}{N_e} \langle \psi_{i_k} | h_k | \psi_{i_k} \rangle = \frac{1}{N_e} N_e \langle \psi_k | h_k | \psi_k \rangle = \langle \psi_k | h_k | \psi_k \rangle$$

$$\epsilon_{i_1 \dots i_k \dots i_{N_e}} \epsilon_{i_1 \dots j_k \dots i_{N_e}} = \sum_{i_k, j_k = 1}^{N_e} (N_e - 1)!\, \epsilon_{123 \dots (N_e - 1)}{}^2 \delta_{i_k j_k} = \sum_{i_k, j_k = 1}^{N_e} (N_e - 1)!\ \delta_{i_k j_k}$$

Hartree-Fock Molecular Orbital Theory: A Variational Mean Field Method

Variational Problem: Variational Calculation

$$E_e[\{\psi_i\}] \equiv \langle \Psi | \hat{H}_e | \Psi \rangle = \left\langle \Psi \middle| \sum_{i=1}^{N_e} h_i + \sum_{i>j}^{N_e} v_{ij} \middle| \Psi \right\rangle = \sum_{i=1}^{N_e} \langle \Psi | h_i | \Psi \rangle + \sum_{i>j}^{N_e} \langle \Psi | v_{ij} | \Psi \rangle$$

$$\langle \Psi | v_{km} | \Psi \rangle = \int dr_1 dr_2 \dots dr_{N_e} \frac{1}{N_e!} \epsilon_{i_1 i_2 \dots i_{N_e}} \psi_{i_1}^\dagger(r_1,\sigma_1) \psi_{i_2}^\dagger(r_2,\sigma_2) \dots \psi_{i_{N_e}}^\dagger(r_{N_e},\sigma_{N_e}) v_{km} \epsilon_{j_1 j_2 \dots j_{N_e}} \psi_{j_1}(r_1,\sigma_1)$$

$$\psi_{j_2}(r_2,\sigma_2) \dots \psi_{j_{N_e}}(r_{N_e},\sigma_{N_e}) = \frac{1}{N_e!} \epsilon_{i_1 i_2 \dots i_{N_e}} \epsilon_{j_1 j_2 \dots j_{N_e}} \left[\int dr_1\, \psi_{i_1}^\dagger(r_1,\sigma_1) \psi_{j_1}(r_1,\sigma_1) \right] \dots$$

$$\left[\int dr_k\, dr_m \psi_{i_k}^\dagger(r_k,\sigma_k) \psi_{i_m}^\dagger(r_m,\sigma_m) v_{km} \psi_{j_k}(r_k,\sigma_k) \psi_{j_m}(r_m,\sigma_m) \right] \dots \left[\int dr_{N_e}\, \psi_{i_{N_e}}^\dagger(r_{N_e},\sigma_{N_e}) \psi_{j_{N_e}}(r_{N_e},\sigma_{N_e}) \right]$$

$$= \frac{1}{N_e!} \epsilon_{i_1 i_2 \dots i_{N_e}} \epsilon_{j_1 j_2 \dots j_{N_e}} \langle \psi_{i_1} | \psi_{j_1} \rangle \dots \langle \psi_{i_k} \psi_{i_m} | v_{km} | \psi_{j_k} \psi_{j_m} \rangle \dots \left\langle \psi_{i_{N_e}} \middle| \psi_{j_{N_e}} \right\rangle$$

$$= \frac{1}{N_e!} \epsilon_{i_1 i_2 \dots i_{N_e}} \epsilon_{j_1 j_2 \dots j_{N_e}} \delta_{i_1 j_1} \dots \langle \psi_{i_k} \psi_{i_m} | v_{km} | \psi_{j_k} \psi_{j_m} \rangle \dots \delta_{i_{N_e} j_{N_e}} = \frac{1}{N_e!} \epsilon_{i_1 \dots i_k, \dots i_m \dots i_{N_e}} \epsilon_{i_1 \dots j_k \dots j_m \dots i_{N_e}} \langle \psi_{i_k} \psi_{i_m} | v_{km} | \psi_{j_k} \psi_{j_m} \rangle$$

$$= \sum_{i_k \neq i_m, j_k \neq j_m}^{N_e} \frac{1}{N_e(N_e-1)} \left(\delta_{i_k j_k} \delta_{i_m j_m} - \delta_{i_k j_m} \delta_{i_m j_k} \right) \langle \psi_{i_k} \psi_{i_m} | v_{km} | \psi_{j_k} \psi_{j_m} \rangle$$

$$= \sum_{i_k \neq i_m}^{N_e} \frac{1}{N_e(N_e-1)} \left[\langle \psi_{i_k} \psi_{i_m} | v_{km} | \psi_{i_k} \psi_{i_m} \rangle - \langle \psi_{i_k} \psi_{i_m} | v_{km} | \psi_{i_m} \psi_{i_k} \rangle \right] = \langle \psi_k \psi_m | v_{km} | \psi_k \psi_m \rangle - \langle \psi_k \psi_m | v_{km} | \psi_m \psi_k \rangle$$

$$\epsilon_{i_1 \dots i_k, \dots i_m \dots i_{N_e}} \epsilon_{i_1 \dots j_k \dots j_m \dots i_{N_e}} = \sum_{i_k \neq i_m, j_k \neq j_m}^{N_e} (N_e - 2)!\, \epsilon_{123 \dots (N_e-2)}{}^2 \left(\delta_{i_k j_k} \delta_{i_m j_m} - \delta_{i_k j_m} \delta_{i_m j_k} \right) = \sum_{i_k \neq i_m, j_k \neq j_m}^{N_e} (N_e - 2)!\, \left(\delta_{i_k j_k} \delta_{i_m j_m} - \delta_{i_k j_m} \delta_{i_m j_k} \right)$$

Hartree-Fock Molecular Orbital Theory: A Variational Mean Field Method

Variational Problem: Variational Calculation

$$E_e[\{\psi_i\}] \equiv \langle \Psi | \hat{H}_e | \Psi \rangle = \left\langle \Psi \middle| \sum_{i=1}^{N_e} h_i + \sum_{i>j}^{N_e} v_{ij} \middle| \Psi \right\rangle = \sum_{i=1}^{N_e} \langle \Psi | h_i | \Psi \rangle + \sum_{i>j}^{N_e} \langle \Psi | v_{ij} | \Psi \rangle$$

$$= \sum_{k=1}^{N_e} \langle \psi_k | h_k | \psi_k \rangle + \sum_{k>m}^{N_e} [\langle \psi_k \psi_m | v_{km} | \psi_k \psi_m \rangle - \langle \psi_k \psi_m | v_{km} | \psi_m \psi_k \rangle]$$

$$\langle \psi_k | h_k | \psi_k \rangle \equiv \int dr_k \, \psi_k^\dagger(r_k, \sigma_k) h_k \psi_k(r_k, \sigma_k)$$

$$\langle \psi_k \psi_m | v_{km} | \psi_k \psi_m \rangle \equiv \int dr_k \, dr_m |\psi_k(r_k, \sigma_k)|^2 v_{km} |\psi_m(r_m, \sigma_m)|^2$$

$$\langle \psi_k \psi_m | v_{km} | \psi_m \psi_k \rangle \equiv \int dr_k \, dr_m \psi_k^\dagger(r_k, \sigma_k) \psi_m^\dagger(r_m, \sigma_m) v_{km} \psi_m(r_k, \sigma_k) \psi_k(r_m, \sigma_m)$$

$$\mathcal{L}[\{\psi_i\}] \equiv E_e[\{\psi_i\}] - \sum_{i,j} \epsilon_{ij} \left(\langle \psi_i | \psi_j \rangle - \delta_{ij} \right) = \sum_{i=1}^{N_e} \langle \psi_i | h_i | \psi_i \rangle$$

$$+ \frac{1}{2} \sum_{i,j}^{N_e} [\langle \psi_i \psi_j | v_{ij} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | v_{ij} | \psi_j \psi_i \rangle] - \sum_{i,j} \epsilon_{ij} \left(\langle \psi_i | \psi_j \rangle - \delta_{ij} \right)$$

Hartree-Fock Molecular Orbital Theory: A Variational Mean Field Method

Variational Problem: Variational Calculation

$$\mathcal{L}[\{\psi_i\}] \equiv E_e[\{\psi_i\}] - \sum_{i,j} \epsilon_{ij} \left(\langle \psi_i | \psi_j \rangle - \delta_{ij}\right) = \sum_{i=1}^{N_e} \langle \psi_i | h_i | \psi_i \rangle$$

$$+ \frac{1}{2} \sum_{i,j}^{N_e} \left[\langle \psi_i \psi_j | v_{ij} | \psi_i \psi_j \rangle - \langle \psi_i \psi_j | v_{ij} | \psi_j \psi_i \rangle\right] - \sum_{i,j} \epsilon_{ij} \left(\langle \psi_i | \psi_j \rangle - \delta_{ij}\right)$$

$$\psi_i^\dagger \to \psi_i^\dagger + \delta\psi_i^\dagger$$

$$\delta\mathcal{L}[\{\psi_i\}] = \int dr_i \sum_{i=1}^{N_e} \delta\psi_i^\dagger(r_i, \sigma_i) h_i \psi_i(r_i, \sigma_i) + \int dr_i \sum_{i}^{N_e} \delta\psi_i^\dagger(r_i, \sigma_i) \sum_{j}^{N_e} \int dr_j\, \psi_i(r_i, \sigma_i) v_{ij} |\psi_j(r_j, \sigma_j)|^2$$

$$- \int dr_i \sum_{i}^{N_e} \delta\psi_i^\dagger(r_i, \sigma_i) \sum_{j}^{N_e} \int dr_j\, \psi_j^\dagger(r_j, \sigma_j) v_{ij} \psi_j(r_i, \sigma_i) \psi_i(r_j, \sigma_j) - \int dr_i \sum_{i=1}^{N_e} \delta\psi_i^\dagger(r_i, \sigma_i) \sum_{j}^{N_e} \epsilon_{ij} \psi_j(r_i, \sigma_i)$$

$$- \sum_{i,j} \delta\epsilon_{ij} \left(\langle \psi_i | \psi_j \rangle - \delta_{ij}\right) = 0$$

$$h_i \psi_i(r_i, \sigma_i) + \left[\sum_{j}^{N_e} \int dr_j\, v_{ij} |\psi_j(r_j, \sigma_j)|^2\right] \psi_i(r_i, \sigma_i) - \sum_{j}^{N_e} \int dr_j\, \psi_j^\dagger(r_j, \sigma_j) \psi_i(r_j, \sigma_j) v_{ij} \psi_j(r_i, \sigma_i) - \sum_{j}^{N_e} \epsilon_{ij} \psi_j(r_i, \sigma_i) = 0$$

$$\langle \psi_i | \psi_j \rangle = \delta_{ij} \qquad (1)$$

Hartree-Fock Molecular Orbital Theory: A Variational Mean Field Method

Variational Problem: Variational Calculation

Similarly, $\boldsymbol{\psi_i \to \psi_i + \delta\psi_i}$ $\qquad \delta\mathcal{L}[\{\boldsymbol{\psi_i}\}] = 0$

$$\boldsymbol{h_i\psi_i(r_i,\sigma_i) + \left[\sum_j^{N_e}\int dr_j\, v_{ij}|\psi_j(r_j,\sigma_j)|^2\right]\psi_i(r_i,\sigma_i) - \sum_j^{N_e}\int dr_j\, \psi_j^\dagger(r_j,\sigma_j)\psi_i(r_j,\sigma_j)v_{ij}\psi_j(r_i,\sigma_i) - \sum_j^{N_e}\epsilon_{ji}^*\psi_j(r_i,\sigma_i) = 0}$$

$$\boldsymbol{\langle\psi_i|\psi_j\rangle = \delta_{ij}}$$

(1)=(2) ➡ $\boldsymbol{\epsilon_{ji}^* = \epsilon_{ij}}$ **Self-adjoint or Hermitian**

$\forall$ **Unitary transformation** $\boldsymbol{U}$, $\boldsymbol{\psi_i \to \widetilde{\psi_i} = U_{ij}\psi_j}$ $\qquad \boldsymbol{\epsilon_{ij} \to \widetilde{\epsilon_{ij}} = U_{ik}\epsilon_{km}(U^{-1})_{mj} = \widetilde{\epsilon}_i\,\delta_{ij}}$ **Diagonalized!**

(1),(2) ➡ **Hartree-Fock Equation**

$$\boldsymbol{h_i\psi_i(r_i,\sigma_i) + \left[\sum_j^{N_e}\int dr_j\, v_{ij}|\psi_j(r_j,\sigma_j)|^2\right]\psi_i(r_i,\sigma_i) - \sum_j^{N_e}\int dr_j\, \psi_j^\dagger(r_j,\sigma_j)\psi_i(r_j,\sigma_j)v_{ij}\psi_j(r_i,\sigma_i) = \epsilon_i\psi_i(r_i,\sigma_i)}$$

For convenience, symbols $\widetilde{\psi_i}$ ***and*** $\widetilde{\epsilon_{ij}}$ ***have been changed back into*** ψ_i ***and*** ϵ_{ij}

Hartree-Fock Molecular Orbital Theory: A Variational Mean Field Method

Koopmans Theorem

Born-Oppenheimer Approximation

Born-Oppenheimer Approximation: Separate Electronic and Nuclear Motion

A General Many-Body Problem:

1) N nuclei described by coordinates $\boldsymbol{R} \equiv \{\boldsymbol{R_1}, \boldsymbol{R_2}, \dots, \boldsymbol{R_N}\}$, momenta $\boldsymbol{P} \equiv \{\boldsymbol{P_1}, \boldsymbol{P_2}, \dots, \boldsymbol{P_N}\}$ and masses $\{\boldsymbol{M_1}, \boldsymbol{M_2}, \dots, \boldsymbol{M_N}\}$
2) N_e electrons described by coordinates $\boldsymbol{r} \equiv \{\boldsymbol{r_1}, \boldsymbol{r_2}, \dots, \boldsymbol{r_{N_e}}\}$, momenta $\boldsymbol{p} \equiv \{\boldsymbol{p_1}, \boldsymbol{p_2}, \dots, \boldsymbol{p_{N_e}}\}$, spins $\boldsymbol{s} \equiv \{\boldsymbol{s_1}, \boldsymbol{s_2}, \dots, \boldsymbol{s_{N_e}}\}$ and masses $\{\boldsymbol{m_1}, \boldsymbol{m_2}, \dots, \boldsymbol{m_{N_e}}\}$
3) Hamiltonian: $\boldsymbol{H = T_N(R) + T_e(r) + V_{NN}(R) + V_{eN}(r, R) + V_{ee}(r)}$

Where nuclei's kinetic energy $T_N(\boldsymbol{R}) \equiv \sum_{I=1}^{N} \frac{\boldsymbol{P_I^2}}{2M_I}$; Electrons' kinetic energy $T_e(\boldsymbol{r}) \equiv \sum_{i=1}^{N_e} \frac{\boldsymbol{p_i^2}}{2m_i}$

Nucleus-nucleus Coulomb Potential $V_{NN}(\boldsymbol{R}) \equiv \frac{1}{2}\sum_{I,J}^{N} \frac{Z_I Z_J e^2}{|\boldsymbol{R_I} - \boldsymbol{R_J}|} = \sum_{I>J}^{N} \frac{Z_I Z_J e^2}{|\boldsymbol{R_I} - \boldsymbol{R_J}|}$ *$Z_I e$: the charge of the nucleus located at $\boldsymbol{R_I}$*

Nucleus- electron Coulomb Potential $V_{eN}(\boldsymbol{r}, \boldsymbol{R}) \equiv -\sum_{I,i}^{N.N_e} \frac{Z_I e^2}{|\boldsymbol{R_I} - \boldsymbol{r_i}|}$

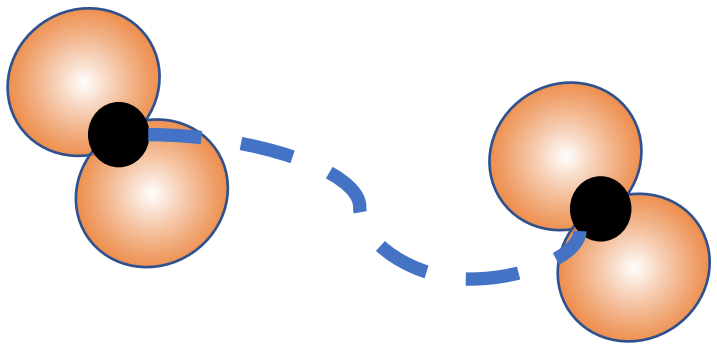
Electron- electron Coulomb Potential $V_{ee}(\boldsymbol{r}) \equiv \frac{1}{2}\sum_{i,j}^{N_e} \frac{e^2}{|\boldsymbol{r_i} - \boldsymbol{r_j}|} = \sum_{i>j}^{N_e} \frac{e^2}{|\boldsymbol{r_i} - \boldsymbol{r_j}|}$

Impossible to solve directly when $N, N_e \gg 1$!

Born-Oppenheimer Approximation: Separate Electronic and Nuclear Motion

Approximations:

1) **Born-Oppenheimer Approximation**
2) **Hartree-Fock Approximation**



$\frac{m_e}{M_n} < 10^{-2} \ll 1$ ➡ Electrons motion time scare $\ll$ Nuclei motion time scale

➡ **1. (1.1)Electrons follow the nuclear motion adiabatically and are dragged by the nuclei without a finite relaxation time; (1.2)Electronic wave function depends on the nuclear positions but not their velocities**

2. (2.1)Nuclear wave functions are relatively spatially localized and more like a point classical particle; (2.2) The nuclear motion sees a smeared-out potential from the speedy electrons

$$H(r,R) = H_e(r,R) + H_N(R);\ H_e(r,R) \equiv T_e(r) + V_{eN}(r,R) + V_{ee}(r), H_N(R) \equiv T_N(R) + V_{NN}(R)$$

$$H(r,R)\Psi(r,R) = E_{tot}\Psi(r,R) \quad \Psi(r,R) \equiv \phi_e(r,R)\phi_N(R) \quad H_e(r,R)\phi_e(r,R) = E_e\phi_e(r,R)$$

Born-Oppenheimer Approximation: Separate Electronic and Nuclear Motion

$$H(r,R)\Psi(r,R) = E_{tot}\Psi(r,R) \qquad \Psi(r,R) \equiv \phi_e(r,R)\phi_N(R) \qquad H_e(r,R)\phi_e(r,R) = E_e\phi_e(r,R)$$

$$H_N(R)\phi_N(R) = (E_{tot} - E_e)\phi_N(R) \quad \Leftrightarrow \quad \phi_e(r,R)H_N(R)\phi_N(R) = (E_{tot} - E_e)\Psi(r,R)$$

$$\Leftrightarrow \quad \phi_e(r,R)H_N(R)\phi_N(R) = \big(H(r,R) - H_e(r,R)\big)\Psi(r,R) = H_N(R)\phi_e(r,R)\phi_N(R)$$

$$\Leftrightarrow \quad T_N(R)\phi_e(r,R)\phi_N(R) = \phi_e(r,R)T_N(R)\phi_N(R) \qquad H_N(R)\phi_e(r,R)\phi_N(R) = (T_N(R) + V_{NN}(R))\phi_e(r,R)\phi_N(R)$$

$$\Leftrightarrow \quad -\hbar^2\sum_{I=1}^{N}\frac{\nabla_I^2}{2M_I}\phi_e(r,R)\phi_N(R) = -\hbar^2\sum_{I=1}^{N}\frac{1}{2M_I}\left[\phi_N(R)\nabla_I^2\phi_e(r,R) + 2\nabla_I\phi_e(r,R)\nabla_I\phi_N(R) + \phi_e(r,R)\nabla_I^2\phi_N(R)\right]$$

$$= -\hbar^2\sum_{I=1}^{N}\frac{1}{2M_I}\phi_e(r,R)\nabla_I^2\phi_N(R)$$

$$\Leftrightarrow \quad -\hbar^2\sum_{I=1}^{N}\frac{1}{2M_I}\left[\phi_N(R)\nabla_I^2\phi_e(r,R) + 2\nabla_I\phi_e(r,R)\nabla_I\phi_N(R)\right] = 0$$

Born-Oppenheimer Approximation

$$\left|\frac{-\hbar^2}{2M_I}\nabla_I^2\phi_e(r,R)\right| \approx \left|\frac{-\hbar^2}{2M_I}\nabla_r^2\phi_e(r,R)\right| \approx \left|\frac{m_e}{M_I}\frac{p_e^2}{2m_e}\right| \ll \left|\frac{p_e^2}{2m_e}\right|$$

$$\left|\frac{-\hbar^2}{M_I}\nabla_I\phi_e(r,R)\nabla_I\phi_N(R)\right| \approx \left|\frac{-\hbar^2}{M_I}\nabla_r\phi_e(r,R)\nabla_I\phi_N(R)\right| \approx \left|\frac{P_I}{M_I}p_e\right| \ll \left|\frac{{p_e}^2}{m_e}\right|$$

Born-Oppenheimer Approximation: Separate Electronic and Nuclear Motion

Conclusion:

$$\boxed{H(r,R)\Psi(r,R) = E_{tot}\Psi(r,R)} \approx$$

$$\Psi(r,R) \equiv \phi_e(r,R)\phi_N(R)$$

$$\boxed{H_e(r,R)\phi_e(r,R) = E_e\phi_e(r,R)}$$

$$H_N(R)\phi_N(R) = (E_{tot} - E_e)\phi_N(R)$$

$$H_e(r,R) \equiv T_e(r) + V_{eN}(r,R) + V_{ee}(r),$$

$$H_N(R) \equiv T_N(R) + V_{NN}(R)$$

$$T_N(R) \equiv \sum_{I=1}^{N} \frac{P_I^2}{2M_I}; \qquad T_e(r) \equiv \sum_{i=1}^{N_e} \frac{p_i^2}{2m_i}$$

$$V_{NN}(R) \equiv \frac{1}{2}\sum_{I,J}^{N} \frac{Z_I Z_J e^2}{|R_I - R_J|} = \sum_{I>J}^{N} \frac{Z_I Z_J e^2}{|R_I - R_J|}$$

$$V_{eN}(r,R) \equiv -\sum_{I,i}^{N.N_e} \frac{Z_I e^2}{|R_I - r_i|}$$

$$V_{ee}(r) \equiv \frac{1}{2}\sum_{i,j}^{N_e} \frac{e^2}{|r_i - r_j|} = \sum_{i>j}^{N_e} \frac{e^2}{|r_i - r_j|}$$