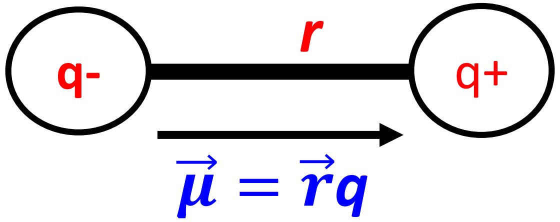
Part III Symmetry and Bonding

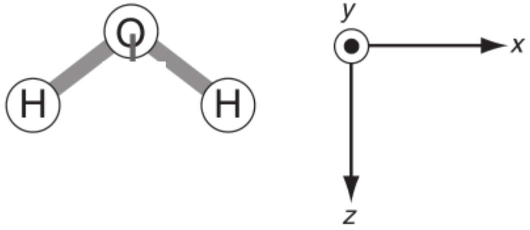
Chapter 8 Miscellany

Prof. Dr. Xin Lu（吕鑫）
Email: xinlu@xmu.edu.cn
http://pcossgroup.xmu.edu.cn/old/users/xlu/group/courses/theochem/

8.1 Dipole moments



$\vec{\mu} = \vec{r}q$



- A (permanent) ***dipole moment*** is a physical property possessed by a molecule.

  e.g., H_2O, define μ (a vector), change upon ***C_z, σ^{xz}*** and ***σ^{yz}*** operations?

  The characters are all +1. Invariant!

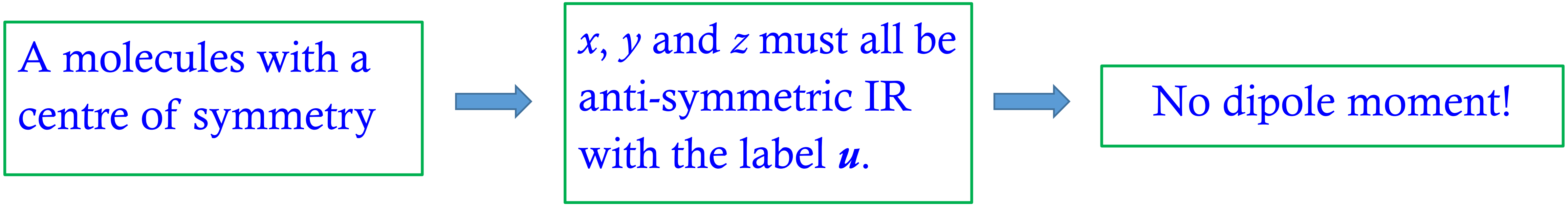
The dipole moment must ***be invariant to symmetry operations possessed by that molecule***!

- The dipole moment must transform as the totally symmetric ***IR***.
- The dipole moment itself is just the result of ***an uneven distribution of charge***, and in general it can only transform like x, y or z.

A molecule possesses a permanent dipole moment only if x, y or z ***transforms as the totally symmetric IR***. (Necessity for the presence of dipole moment!)

8.1 Dipole moments

- e.g., H_2O C_{2v}, z transforms as A_1(the totally symmetric ***IR***) → it has a dipole along z.
- e.g., benzene (D_{6h}), z transforms as A_{2u} and (x,y) transform as E_{1u}. → no dipole.



A molecules with a centre of symmetry

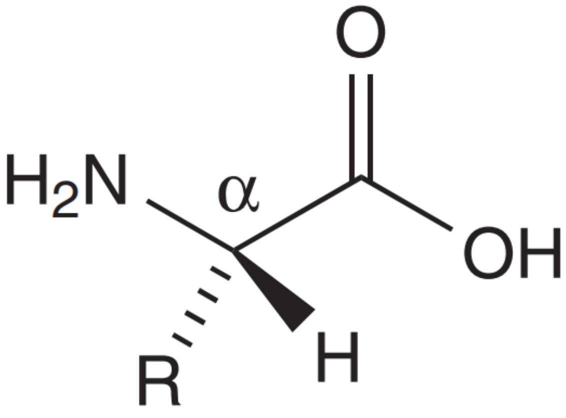
x, y and z must all be anti-symmetric IR with the label ***u***.

No dipole moment!

- Note that this discussion refers to ***the permanent dipole possessed by a molecule in its equilibrium geometry***.

8.2 Chirality

- ***Chiral molecules*** have the physical property that they ***rotate the plane of polarized light***.
- ***A molecule is chiral if it cannot be superimposed on its mirror image***, or, in the language of group theory, if the molecule does not possess any improper axes of rotation, S_n.
- It is important to recall that a *mirror plane* is the same thing as S_1 and a centre of symmetry is the same thing as S_2. Therefore molecules possessing either mirror planes or a centre of symmetry are not chiral.
- If in a molecule having no S_n a carbon atom is attached to four different groups i.e. C(ABCD) then clearly the molecule ***is chiral***. Such a carbon is called a ***chiral centre***.

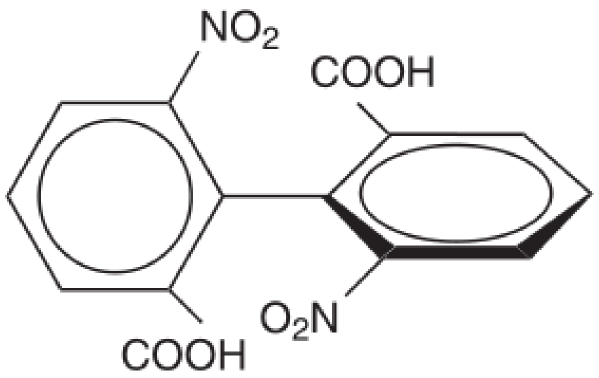


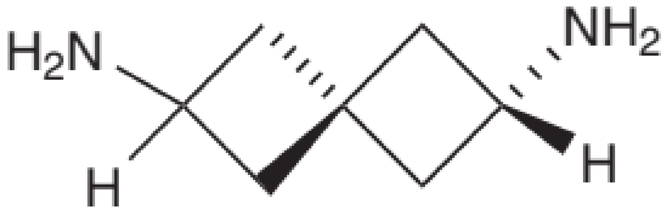
e.g., amino acids with the *α c*arbon in a chiral centre.

8.2 Chirality

- **Generating chirality without use of chiral centres.**

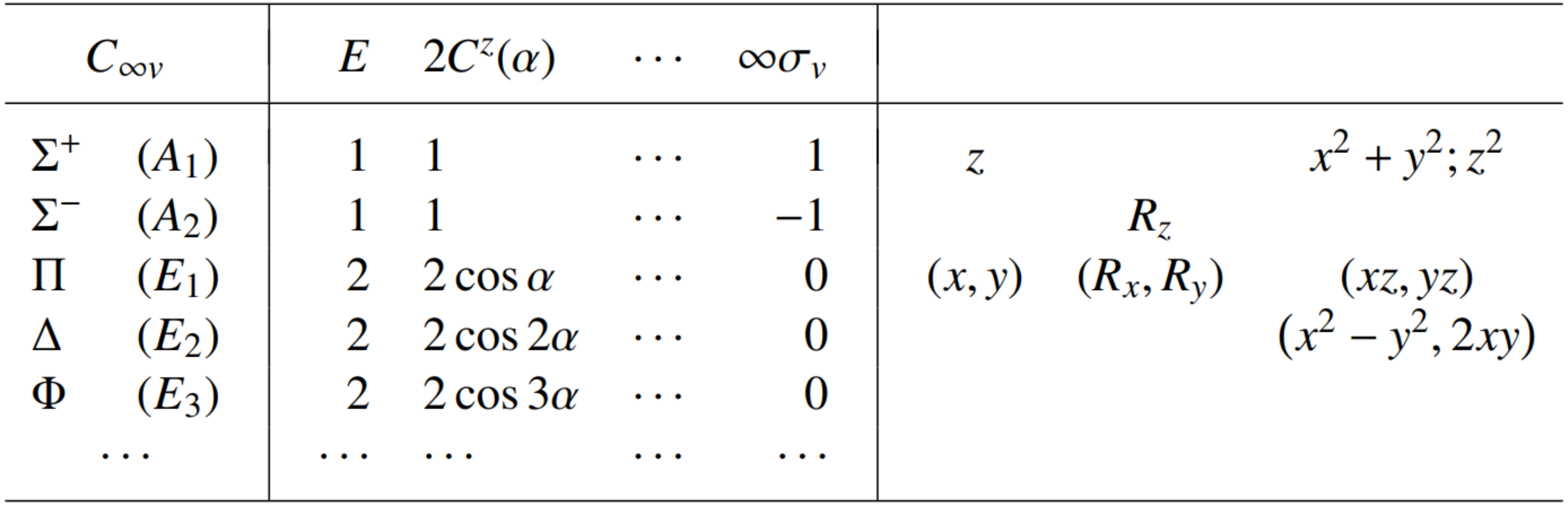
Neither of the molecules shown below have chiral centres, but they are nevertheless chiral as a result of ***restricted rotation about the C–C bond*** in the case of the molecule on the left, and ***the geometry of the fused four-membered rings*** on the right.





8.3 Infinite groups

- *Non-centrosymmetric linear* molecules (e.g. OCS, NNO) ~ $C_{\infty v}$.



$C_{\infty v}$		E	$2C^z(\alpha)$	$\cdots$	$\infty\sigma_v$			
Σ^+	(A_1)	1	1	$\cdots$	1	z		$x^2+y^2; z^2$
Σ^-	(A_2)	1	1	$\cdots$	-1		R_z	
Π	(E_1)	2	$2\cos\alpha$	$\cdots$	0	(x, y)	(R_x, R_y)	(xz, yz)
Δ	(E_2)	2	$2\cos 2\alpha$	$\cdots$	0			$(x^2-y^2, 2xy)$
Φ	(E_3)	2	$2\cos 3\alpha$	$\cdots$	0			
$\cdots$		$\cdots$	$\cdots$	$\cdots$	$\cdots$			

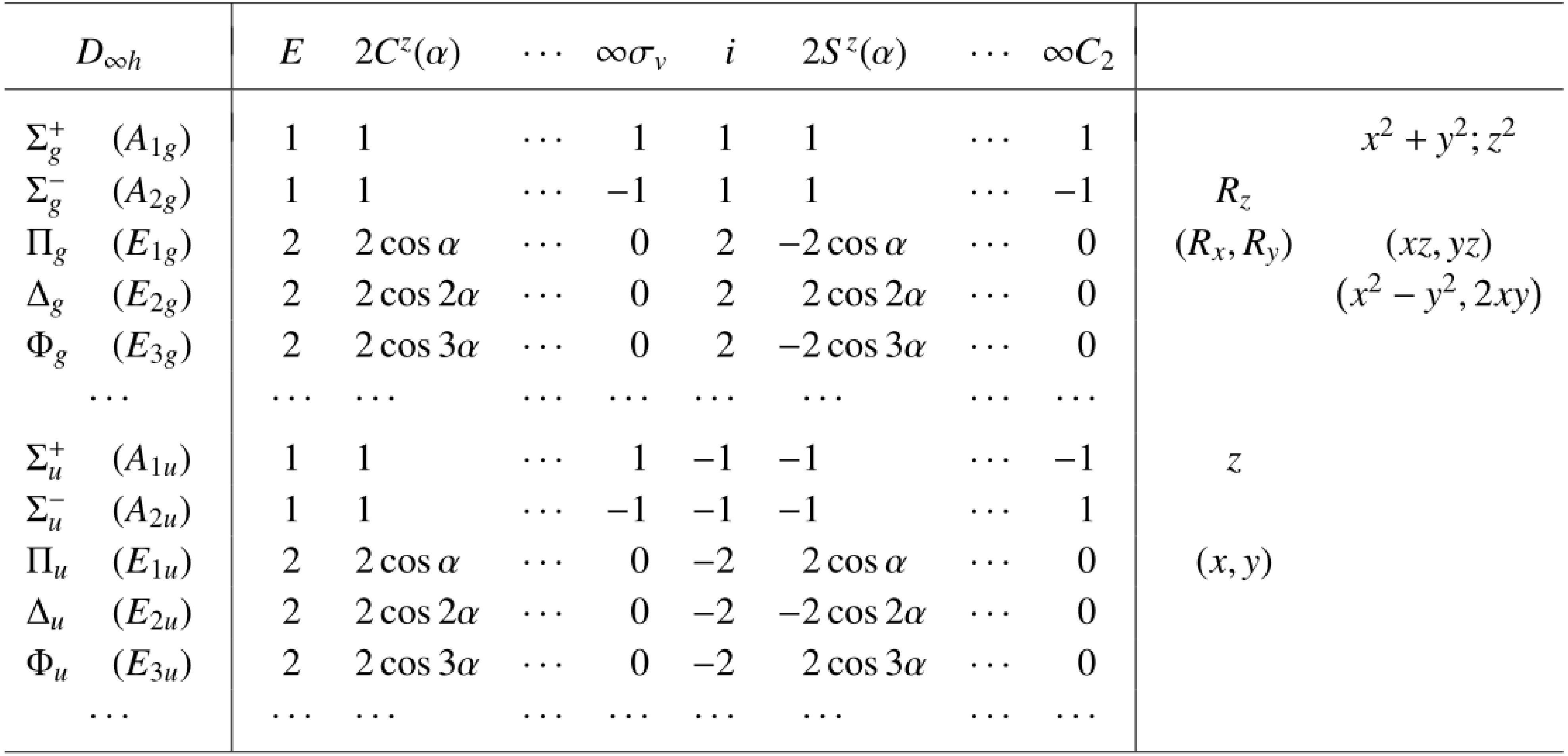
- The long axis of such molecules is the principal axis (z) and a ***rotation*** through ***any angle*** $\boldsymbol{\alpha}$ about this axis is a symmetry operation.

- There are thus an ***infinite number*** of such rotation axes, identified as $C^z(\alpha)$.

- There are an *infinite number of mirror planes* ($\infty\sigma_v$) containing the internuclear axis.

8.3 Infinite groups

- Centrosymmetric linear molecules (e.g. CO_2, BeH_2) ~ $D_{\infty h}$.



$D_{\infty h}$	E	$2C^z(\alpha)$	$\cdots$	$\infty\sigma_v$	i	$2S^z(\alpha)$	$\cdots$	∞C_2		
Σ_g^+ (A_{1g})	1	1	$\cdots$	1	1	1	$\cdots$	1		$x^2+y^2; z^2$
Σ_g^- (A_{2g})	1	1	$\cdots$	-1	1	1	$\cdots$	-1	R_z	
Π_g (E_{1g})	2	$2\cos\alpha$	$\cdots$	0	2	$-2\cos\alpha$	$\cdots$	0	(R_x, R_y)	(xz, yz)
Δ_g (E_{2g})	2	$2\cos 2\alpha$	$\cdots$	0	2	$2\cos 2\alpha$	$\cdots$	0		$(x^2-y^2, 2xy)$
Φ_g (E_{3g})	2	$2\cos 3\alpha$	$\cdots$	0	2	$-2\cos 3\alpha$	$\cdots$	0		
$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$		
Σ_u^+ (A_{1u})	1	1	$\cdots$	1	-1	-1	$\cdots$	-1	z	
Σ_u^- (A_{2u})	1	1	$\cdots$	-1	-1	-1	$\cdots$	1		
Π_u (E_{1u})	2	$2\cos\alpha$	$\cdots$	0	-2	$2\cos\alpha$	$\cdots$	0	(x, y)	
Δ_u (E_{2u})	2	$2\cos 2\alpha$	$\cdots$	0	-2	$-2\cos 2\alpha$	$\cdots$	0		
Φ_u (E_{3u})	2	$2\cos 3\alpha$	$\cdots$	0	-2	$2\cos 3\alpha$	$\cdots$	0		
$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$	$\cdots$		

- ***$C^z(\alpha)$ rotation*** axes, $\infty\sigma_v$, i, ∞C_2 axes, and ***$S^z(\alpha)$ axes***.

8.3 Infinite groups

- As a result of the infinite number of operations contained by these groups it is not quite straightforward to apply the various methods that have been described above for finite groups.

- In these groups a state possessing *a certain amount of angular momentum* about the principal axis transforms as a particular ***IR***. The ***IR*** as which a state transforms is therefore not ***only a symmetry label*** but also ***characterizes the angular momentum***.

8.3 Infinite groups

We can enumerate the particular properties of the ***IR***s and the significance of their labels.

1. One-dimensional ***IR***s are labelled Σ.

2. For Σ ***IR***s, the superscript **+** or **–** indicates the behavior under any one of the σ_v planes:

+ ~symmetric under σ_v (i.e. the character is +1),

– ~antisymmetric under σ_v (i.e. the character is –1).

3. In $D_{\infty h}$, the g or u subscript indicates the symmetry under the ***inversion*** operation:

g ~ symmetric under i (i.e. the character is positive),

u ~ antisymmetric under i (i.e. the character is negative).

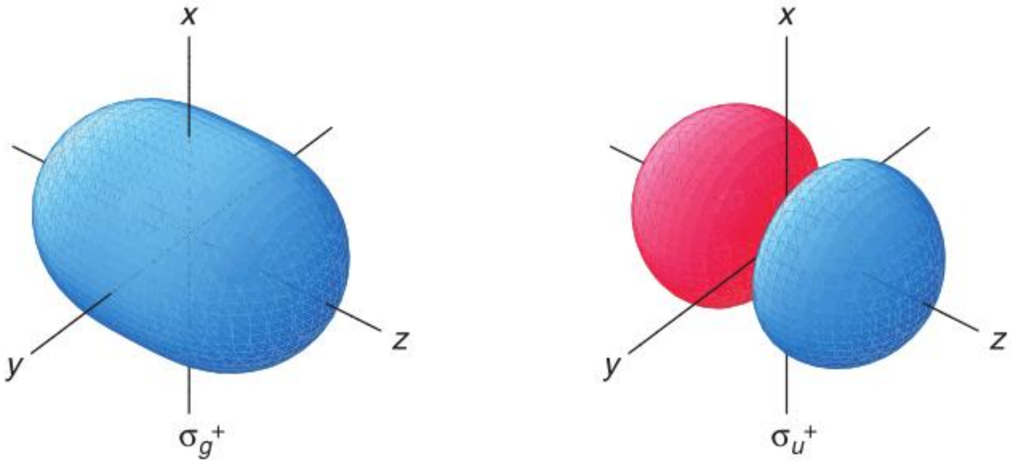
8.3 Infinite groups

4. A ***Σ IR*** indicates that there is no angular momentum about the principal axis.

5. ***Π***, Δ and ***Φ IR***s are all *two-dimensional*; they correspond to ±1, ±2, ±3 units, respectively, of *angular momentum* about the principal axis.

e.g, In H_2^+, the MOs formed from the overlap of two 1s AOs are labelled $\boldsymbol{\sigma}_{\mathbf{g}}^{+}$ and $\boldsymbol{\sigma}_{\mathbf{u}}^{+}$.

- They transform as the *IR*s $\boldsymbol{\Sigma}_{\mathbf{g}}^{+}$ and $\boldsymbol{\Sigma}_{\mathbf{u}}^{+}$, respectively.
- Both are *symmetric* with respect to $\boldsymbol{\sigma_v}$.
- They differ in their symmetry with respect to ***i***.
- Neither orbital has any angular momentum about the principal axis.

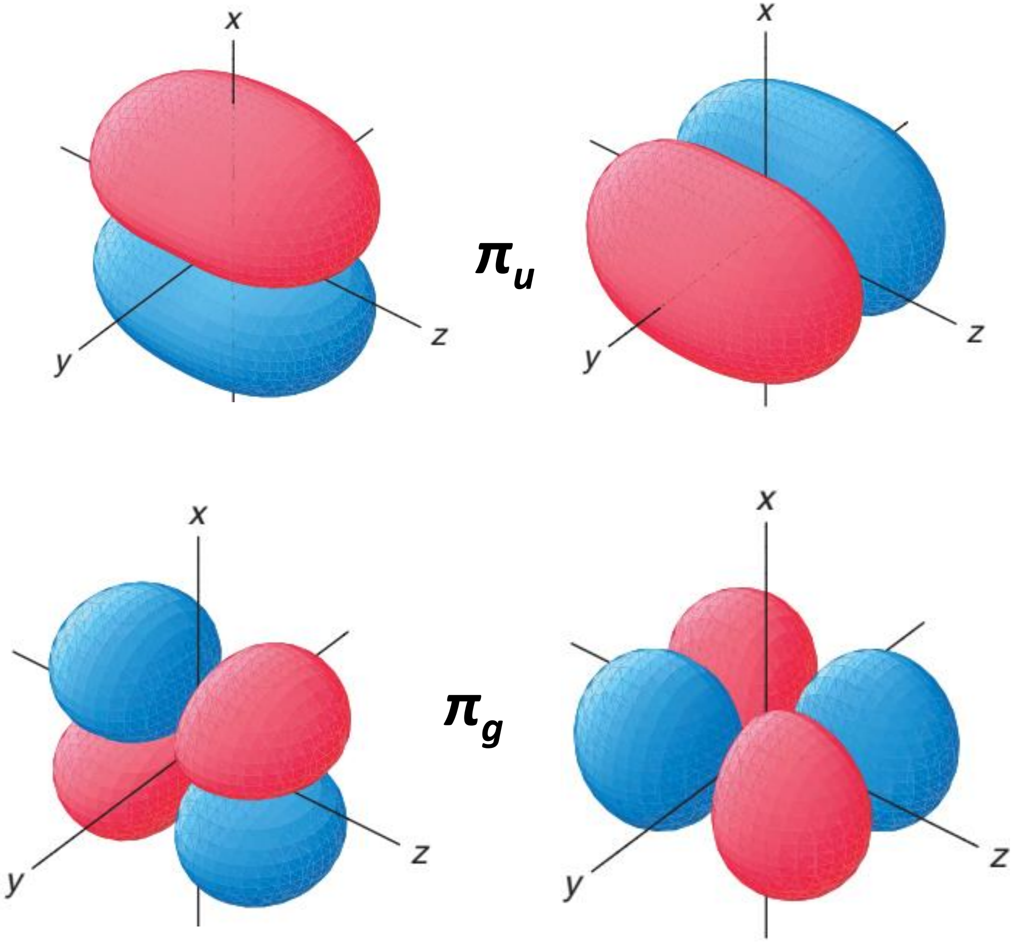


8.3 *Infinite groups*

- Two ***2p*** AOs overlap 'head on' to form two MOs with symmetry labels $\boldsymbol{\sigma_g^+}$ and $\boldsymbol{\sigma_u^+}$.
- If the ***2p*** AOs overlap 'sideways on' the resulting MOs have symmetry labels π_u and π_g.

1) Each is doubly degenerate since there are in fact two pairs of ***p*** orbitals (***two*** $2p_x$ and ***two*** $2p_y$) overlapping.

2) Each MO has ±1 unit of ***angular momentum*** about the principal axis.



GOOD LUCK !

8.4 Allowed transitions in electronic excitation spectrum

- Suppose electronic excitation does not change the spin quantum number (*zero*), we can consider the orbital distribution of electronic density. The symmetry of ***the overall electronic wavefunction*** for a molecule in its *i*th state (ψ_i) is given by the product

$$\Gamma^{i}_{tot} = \Gamma^{(i)}_{SOMO_1} \otimes \Gamma^{(i)}_{SOMO_2} \otimes \cdots \qquad (\Gamma^{(i)}_{SOMO_k} \sim \text{IR for the } k\text{th SOMO})$$

$\Gamma^{i}_{tot} = \Gamma^{tot.sym.}$ for a closed-shell electronic configuration.

- *The transition moment* for transition from states ψ_i to ψ_j is given by

$$R_{ij} = \int \psi_i \hat{\mu} \psi_j \, d\tau \xrightarrow{\text{To be non-zero}} \Gamma_{i\mu j} = \Gamma^{i}_{tot} \otimes \Gamma^{\hat{\mu}} \otimes \Gamma^{j}_{tot} = \Gamma^{tot.sym.} \longrightarrow \Gamma^{i}_{tot} \otimes \Gamma^{j}_{tot} = \Gamma^{\hat{\mu}}$$

- *The criterion for a transition being electric dipole allowed* is that the direct product representation for the two states ψ_i to ψ_j be or contain an ***IR*** to which one or more of Cartesian coordinates belongs to.

8.7 Allowed transitions in electronic excitation spectrum

C_{2v}	E	C_2^z	σ^{xz}	σ^{yz}			
A_1	1	1	1	1	z		$x^2; y^2; z^2$
A_2	1	1	−1	−1		R_z	xy
B_1	1	−1	1	−1	x	R_y	xz
B_2	1	−1	−1	1	y	R_x	yz

- Example 1: **H_2O**

Ground state: $2a_1^2 1b_1^2 3a_1^2 1b_2^2 4a_1^0 2b_1^0$ $\qquad \Gamma_{tot}^{gs} = A_1$

1st excited state: $2a_1^2 1b_1^2 3a_1^2 1b_2^1 4a_1^1 2b_1^0$ $\qquad \Gamma_{tot}^{1es} = B_2 \otimes A_1 = B_2$

$\rightarrow \Gamma_{tot}^{gs} \otimes \Gamma_{tot}^{1es} = B_2 \otimes A_1 = B_2$ *So y belongs to the same IR!* *Allowed transition!*

Q: Is the excitation from $1b_2$ to $2b_1$ allowed?

Elec. config. of the excited state: $2a_1^2 1b_1^2 3a_1^2 1b_2^1 4a_1^0 2b_1^1$

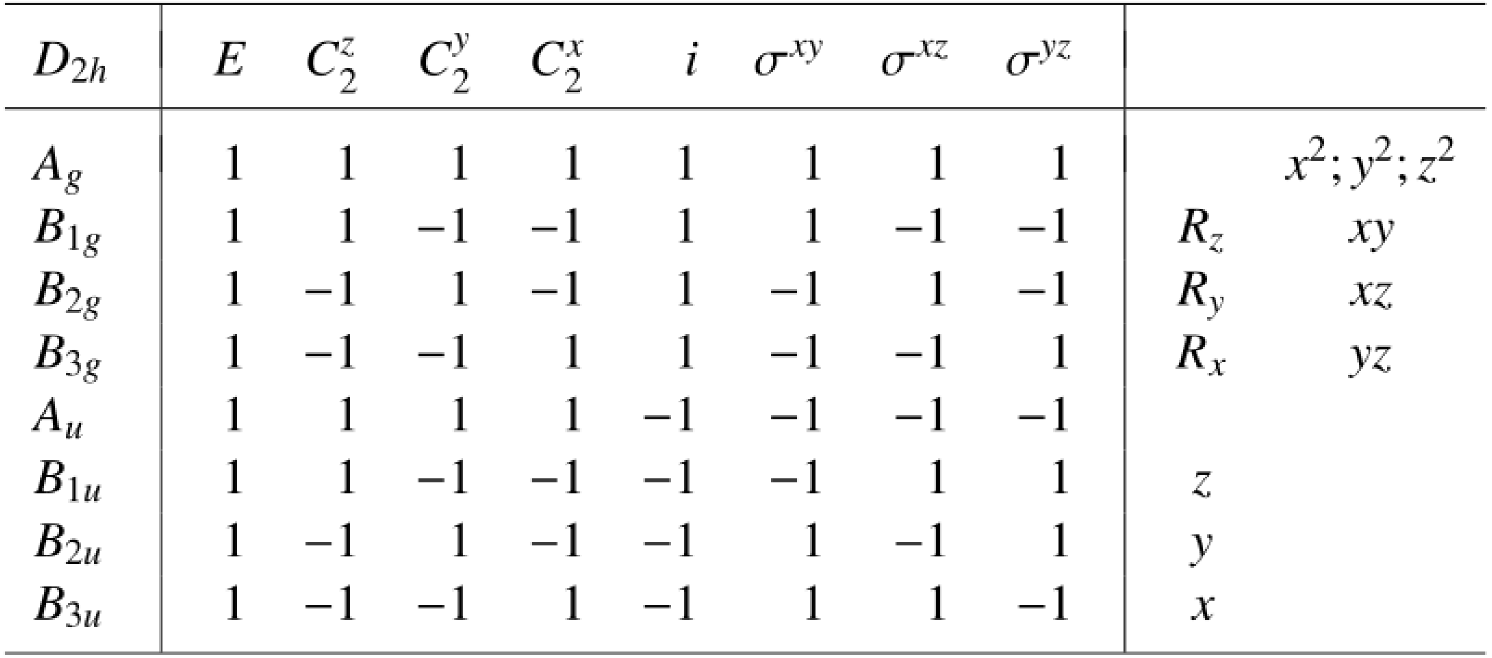
Example 2: **naphthalene**

Ground state: $1b_{1u}^{2}1b_{2g}^{2}1b_{3g}^{2}2b_{1u}^{2}1a_{u}^{2}2b_{2g}^{0}2b_{3g}^{0}$ $\Gamma_{tot}^{gs} = Ag$

1st excited state: $1b_{1u}^{2}1b_{2g}^{2}1b_{3g}^{2}2b_{1u}^{2}1a_{u}^{1}2b_{2g}^{1}2b_{3g}^{0}$ $\Gamma_{tot}^{1es} = ?$

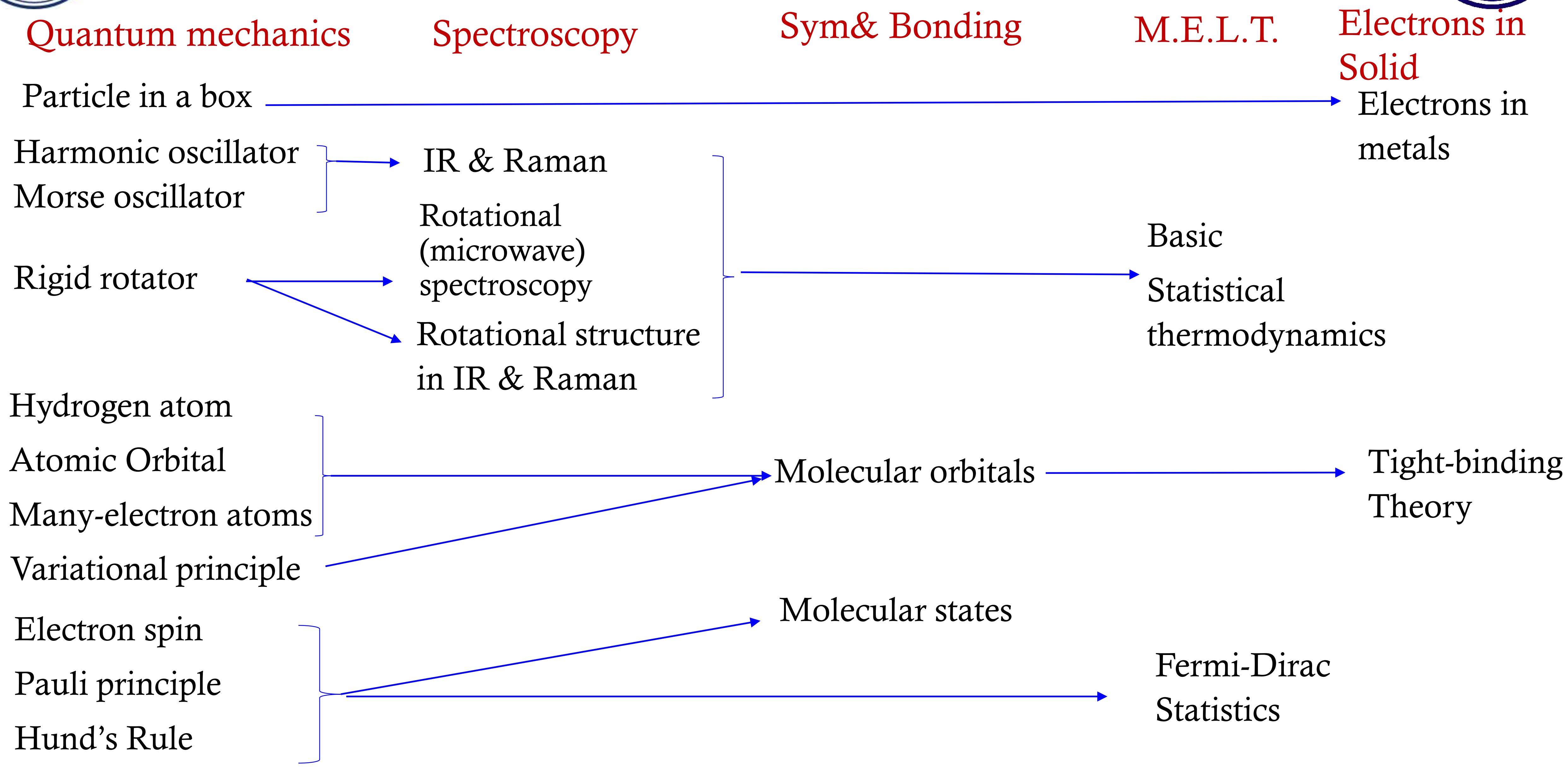
2st excited state: $1b_{1u}^{2}1b_{2g}^{2}1b_{3g}^{2}2b_{1u}^{2}1a_{u}^{1}2b_{2g}^{0}2b_{3g}^{1}$ $\Gamma_{tot}^{2es} = ?$

- **Are the two lowest excitations allowed?**



D_{2h}	E	C_2^z	C_2^y	C_2^x	i	σ^{xy}	σ^{xz}	σ^{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	

Overview of Chemical Theory I&II



Quantum mechanics

Spectroscopy

Sym& Bonding

M.E.L.T.

Electrons in Solid

Particle in a box

Electrons in metals

Harmonic oscillator

Morse oscillator

IR & Raman

Rotational (microwave) spectroscopy

Rigid rotator

Rotational structure in IR & Raman

Basic Statistical thermodynamics

Hydrogen atom

Atomic Orbital

Many-electron atoms

Variational principle

Molecular orbitals

Tight-binding Theory

Electron spin

Pauli principle

Hund’s Rule

Molecular states

Fermi-Dirac Statistics

§ 8.5 Symmetry rules for molecular reactions

Brief introduction:

- ***Frontier Molecular orbital (FMO)*** Theory proposed by K. Fukui in early 1950s. (*J. Chem. Phys.* 1952, 20, 722.)
- ***The Principle of Orbital Symmetry Conservation*** proposed by R.B. Woodward and R. Hoffmann in 1965. (*JACS*, 1965, 87, 395.)
- Owing to their aforementioned contributions, Fukui and Hoffmann were awarded Nobel Prize in Chemistry in 1981.

8.5.1 Frontier molecular orbitals Theory (1951)

- A deeper understanding of chemical reactivity can be gained by focusing on the *frontier orbitals* of the reactants.

- We need to consider only two frontier molecular orbitals (FMO′s), the HOMO and LUMO, to predict the structure of the product.

Highest occupied molecular orbital (HOMO)

Lowest unoccupied molecular orbital (LUMO)

•The FMO theory can be regarded as a natural extension of MO theory that facilitates us to obtain qualitative understanding of chemical reactivity.

Reaction condition

Regio- and stereoselectivity

1. During the course of a chemical reaction, the orbitals that are most readily accessible for interaction are the frontier orbitals.

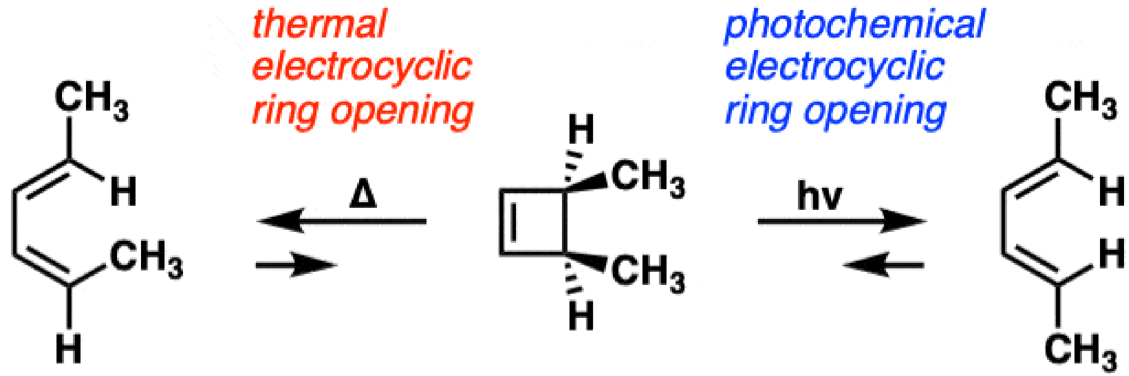
2. When two molecules approach each other, **the symmetry of the HOMO of one molecule must be compatible with that of the LUMO of the other molecule, i.e. orbitals with the same sign will overlap.** This forms a transition state which is relatively stable and is a symmetry-allowed state.

3. **The energy levels of the interacting HOMO and LUMO must be comparable (< 6 eV).**

4. When the HOMO and LUMO of two molecules overlap, electrons are transferred from the HOMO of one molecule to the LUMO of the other molecule. **The direction of the transfer should be in line with the electronegativities** and be consistent with the weakening of the original bond.

Example: electrocyclic reactions

Electrocyclic ring opening: thermal (heat) versus photochemical (hν) conditions give different products (stereoisomers)



cis, trans diene

(2*Z*,4*E*)-2,4-Hexadiene

cis-3,4-dimethyl cyclobutene

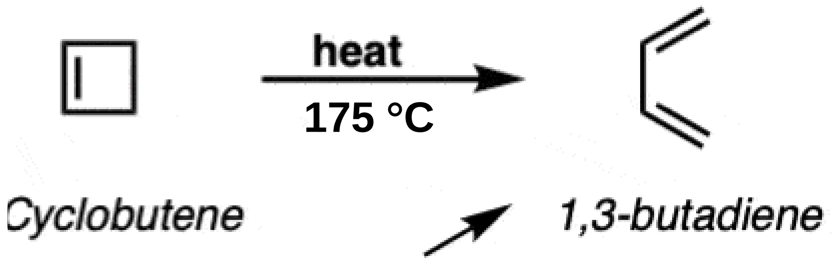
trans, trans diene

(2*E*,4*E*)-2,4-Hexadiene

Summary:

π electrons	conditions	direction
4	thermal (Δ)	conrotatory
4	photochemical (*hν*)	disrotatory

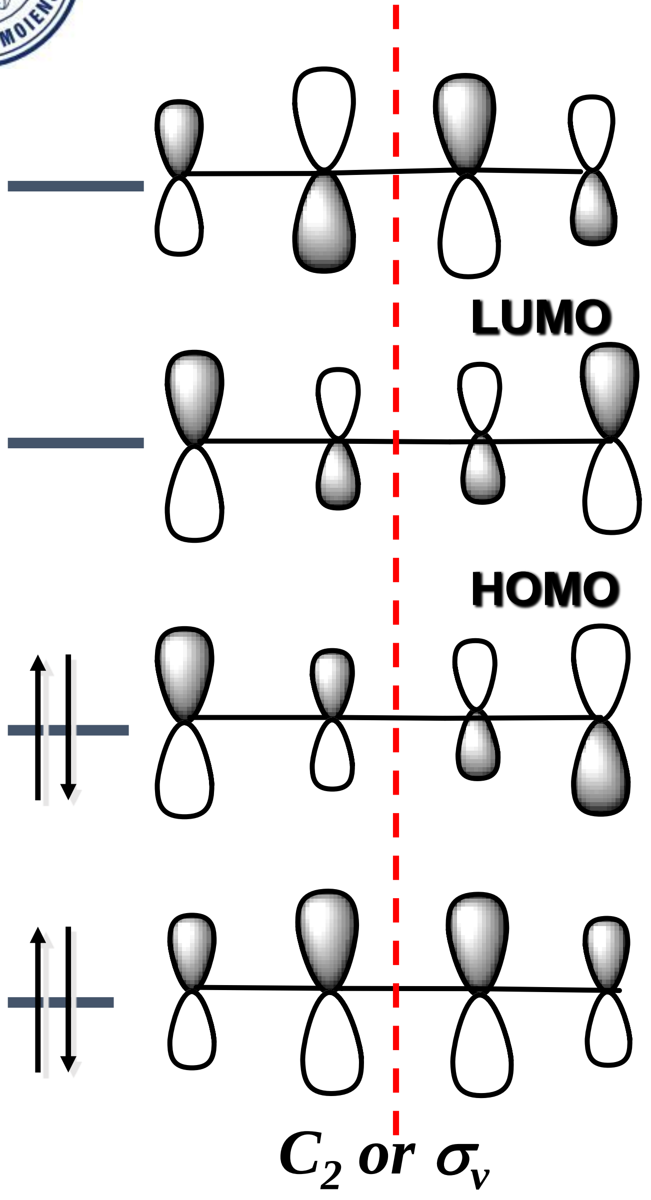
electrocyclic ring-opening (1905)

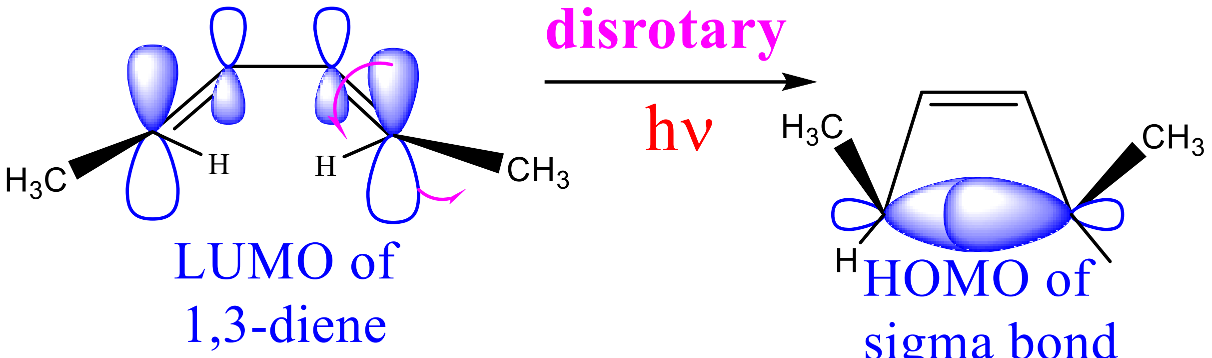


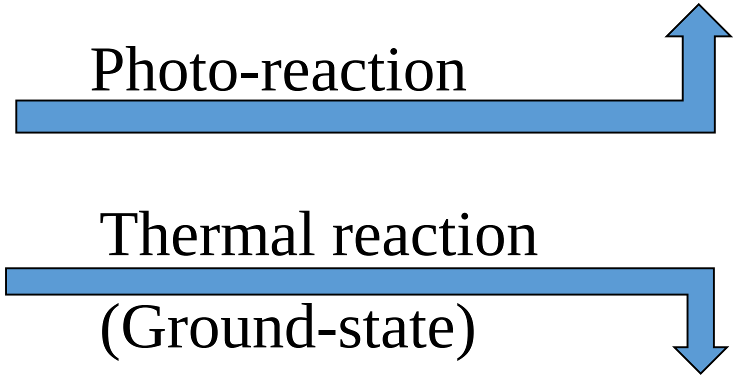
This was unexpected !

- Ring opening: cleavage of a 2c-2e σ bond, 2σe→ 2πe
- Ring closure: 2πe→ 2σe

Example: ***Electrocyclic reaction of 1,3-diene***





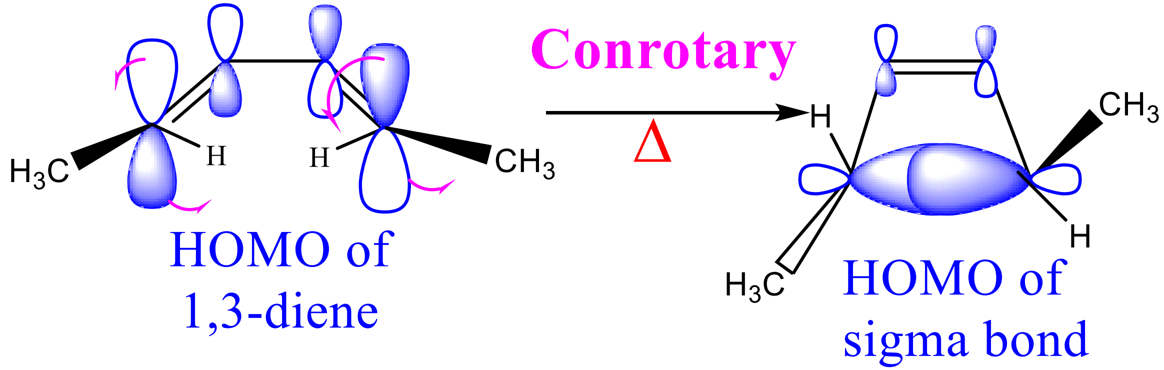


σ_v symmetry maintained!

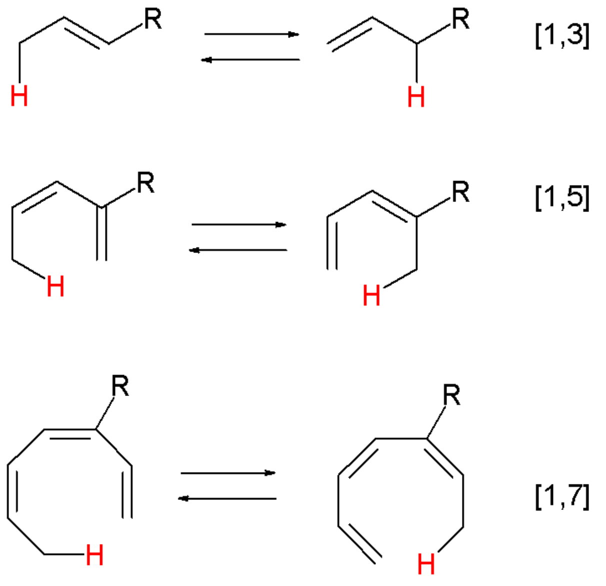
LUMO: σ_v ~ symmetric!

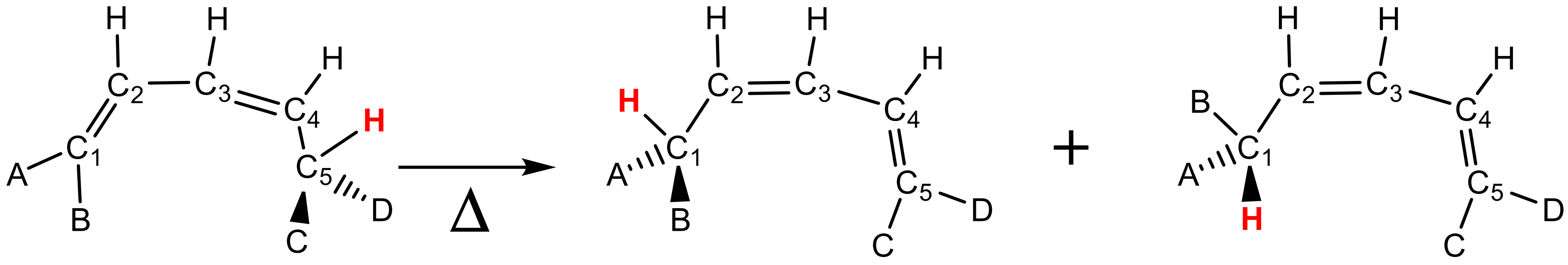
HOMO: C_2 ~ symmetric!

C_2 symmetry maintained!



[1,n] sigmatropic shift : stereochemical rules

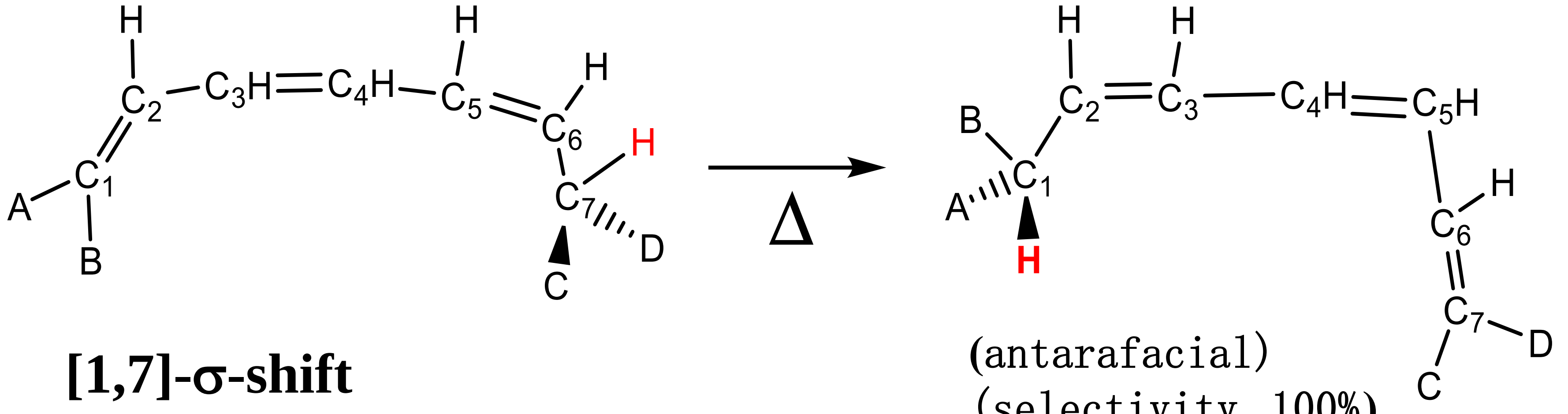




[1,5]-σ-shift

(suprafacial)
(selectivity 100%)

(antarafacial)
(selectivity 0%)



[1,7]-σ-shift

(antarafacial)
(selectivity 100%)

- Hint: Suppose the transition state is a combination of a H atom and a [n]polyene with odd-number p_π orbitals.

[n]Polyenes: *n=odd*

c_i $\sin\theta, \sin 2\theta....$ $\sin(n-1)\theta,\ \sin n\theta$

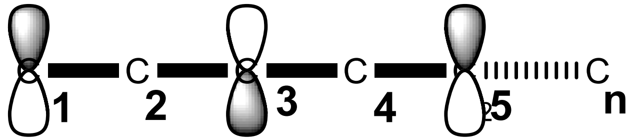
$$\psi = \sum_i c_i\phi_i$$

$$\theta = m\pi/(n+1);\quad E = \alpha + 2\beta\cos\theta \quad (m = 1,2,....n)$$

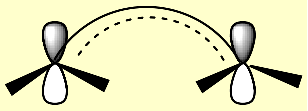
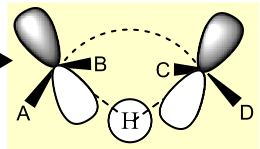
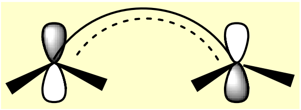
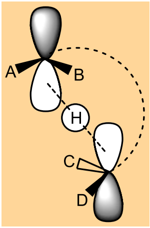
As ***n =odd***, SOMO with ***m = (n+1)/2***,

➡ $\theta_{somo} = \pi/2,\ E_{somo} = \alpha \qquad c_1 = \sin(\pi/2) = 1;\ c_2 = 0;\ c_3 = -1;\ ...,c_n = \sin(n\pi/2)$

$\Rightarrow \psi_{SOMO} = A\sum_{k=1}^{n}(\phi_1 - \phi_3 + \phi_5 - ...) \Rightarrow$



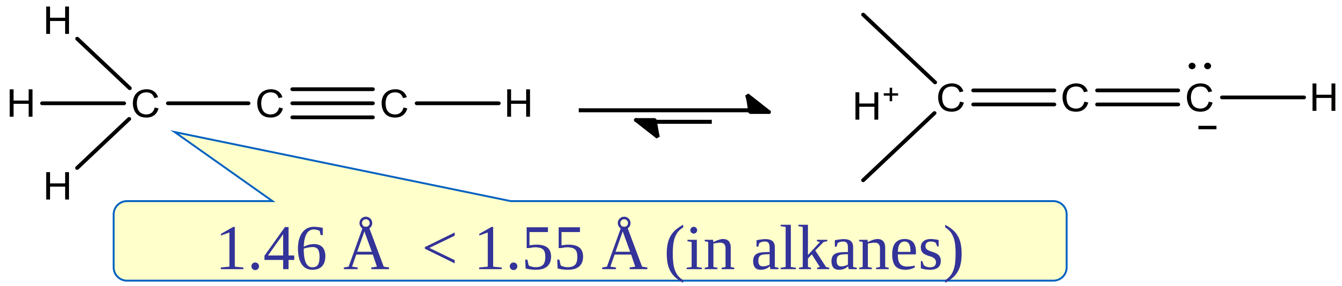
with $c_1 = c_{4k+1} = -c_{4k+3}$

	Symmetry of SOMO			**Sigmatropic shift**		
		σ_v	**C_2**	**TS symmetry**		**Reaction Mode**
n= 4k+1		**Sym**	**Asym**	**σ_v** →		suprafacial
n= 4k+3		**Asym**	**Sym**	**C_2** →		antarafacial

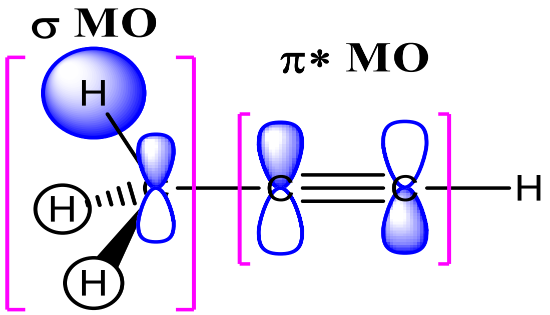
8.4 Hyperconjugation

- First introduced by R.S. Mulliken in 1939.

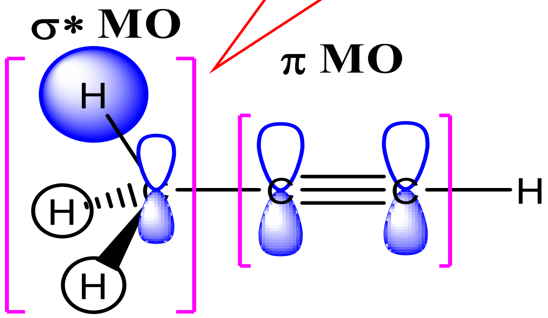
- Hyperconjugation is ***the stabilizing interaction*** of the electrons in a ***σ-bond*** (usually C–H or C–C) with an adjacent empty (or partially filled) ***non-bonding p-orbital or antibonding π orbital***, which gives ***an extended molecular orbital*** that increases the stability of the system.



1.46 Å < 1.55 Å (in alkanes)



Why not ?



- π*(C≡C) is generally lower in energy than the σ*(C-H) of CH$_3$.

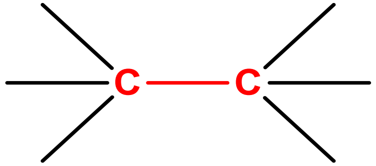
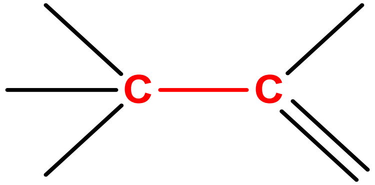
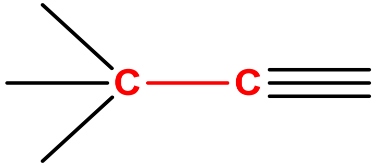
→ π*(C≡C) is more electron-affinitive than the σ*(C-H) of CH$_3$.

σ(C-H) → π*(C≡C) >> π (C≡C)→ σ* (C-H).

Effects of hyperconjugation on Chemical properties

A. Bond length and bond energy:

σ-bond: Shortening of bond length and increasing of bond energy.

Bond type	Hybridization	C-C bond length (Å)	C-C bond energy(kJ.mol^{-1})
	**sp^3-sp^3**	**1.54**	**346.3**
	**sp^3-sp^2**	**1.51**	**357.6**
	**sp^3-sp**	**1.46**	**382.5**

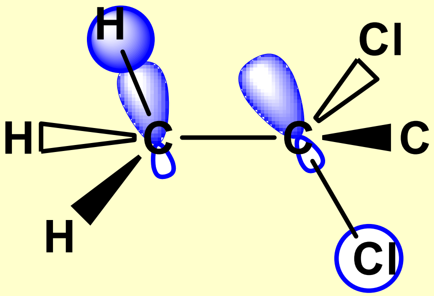
- The π* MO of a C=C bond is generally higher in energy and, hence, less electron-affinitive than that of a C≡C bond.

Effects of hyperconjugation on Chemical properties

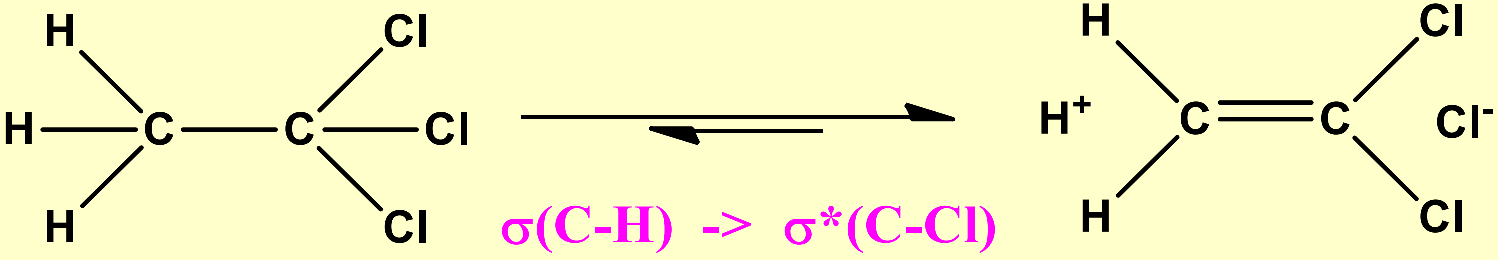
B. Dipole moment

The dipole moment of 1,1,1-trichloroethane with hyperconjugation is much larger than that of chloroform (HCCl$_3$).

LMO picture



σ(C-H) ⟶ σ*(C-Cl)



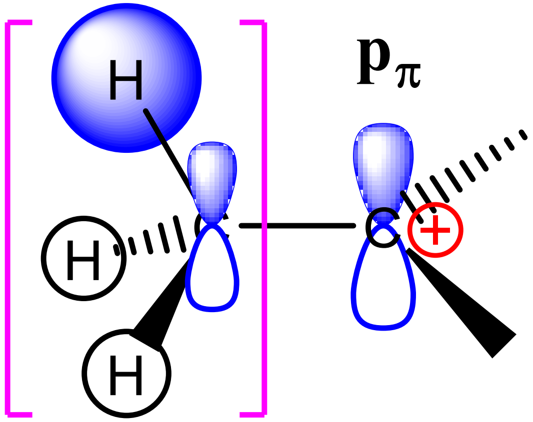
σ(C-H) -> σ*(C-Cl)

C. Stabilizing carbocations

Hyperconjugative interaction between the electron(s) in a bond that is *β* to the positively charged C can stabilize a carbocation.

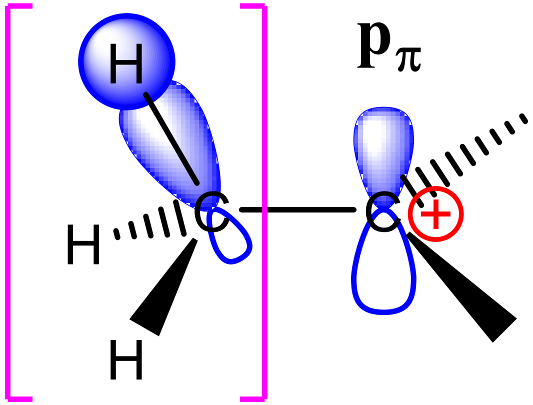
$\sigma(C\text{-}H) \rightarrow p_{\pi}(C^+)$

σ MO of CH_3



1） σ MO of $CH_3 + p_{\pi}\ (C^+)$

σ(C-H) LMO



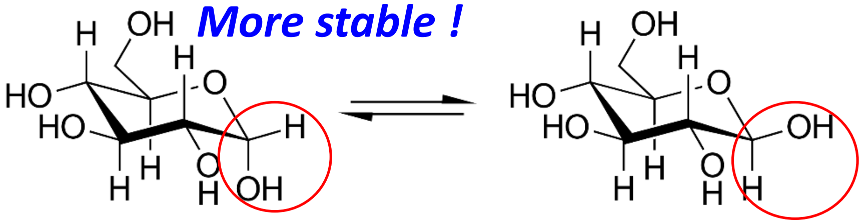
2） a σ(C-H) LMO of $CH_3 + p_{\pi}\ (C^+)$

Stability of carbocations:

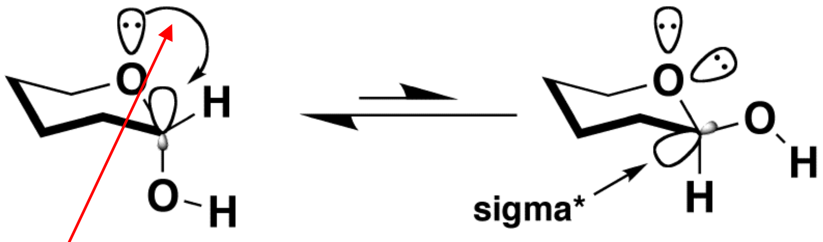
$(CH_3)_3C^+ > (CH_3)_2CH^+ > (CH_3)CH_2^+ > CH_3^+$

Anomeric effect (端基异构效应) & hyperconjugation

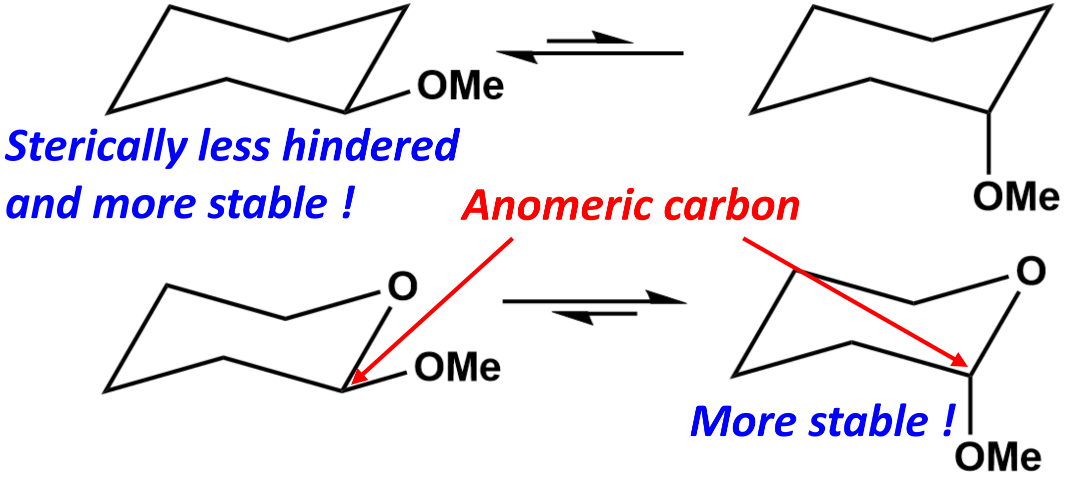
- This effect was originally observed in pyranose rings by ***J. T. Edward*** in 1955 when studying carbohydrate chemistry, but the term was first introduced in 1958.
- The **anomeric effect** or **Edward-Lemieux effect** is a *stereoelectronic effect* that describes the tendency of *heteroatomic substituents* adjacent to *a heteroatom* within a cyclohexane ring to prefer the *axial* orientation instead of the less hindered *equatorial* orientation that would be expected from steric consideration.



α-D-glucopyranose β-D-glucopyranose

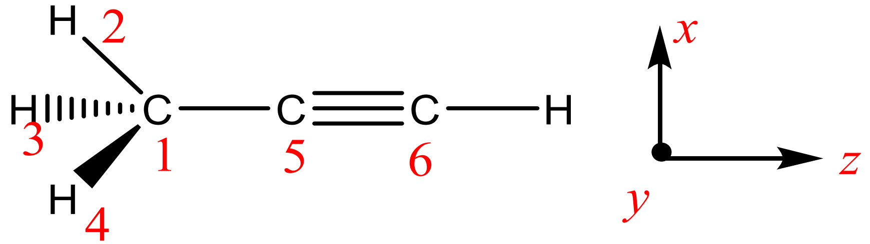


Favored n(O) → σ(C-O) hyperconjugation*



Juaristi, E.; Cuevas, G. *Tetrahedron*. 1992, **48** (24): 5019.

Key valence MOs of the CH_3 and C_2 fragments

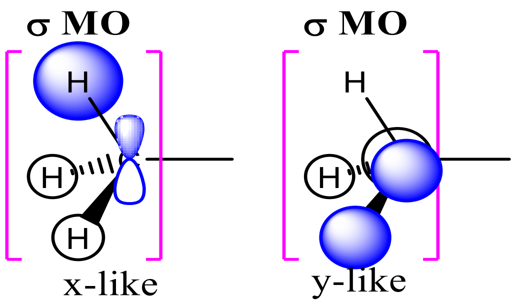


C_{3v}	E	$2C_3$	$3\sigma_v$	Basis components		
A_1	1	1	1	z		x^2+y^2, z^2
A_2	1	1	-1		R_z	
E	2	-1	0	(x,y)	(R_x,R_y)	$(x^2-y^2, xy)(yz,xz)$

- **C_2**: $(p_{x5}, p_{y5}), (p_{x6}, p_{y6}) \sim$ ***E***

$(p_{x5}+p_{x6})/\sqrt{2}$ ~ *x-like*, $(p_{y5}+p_{y6})/\sqrt{2}$ ~ *y-like* ***e (π-bonding)***

$(p_{x5}-p_{x6})/\sqrt{2}$ ~ *x-like*, $(p_{y5}-p_{y6})/\sqrt{2}$ ~ *y-like* ***e* (π-antibonding)***



- **CH_3**: $(p_{x1}, p_{y1}) \sim$ ***E***

SOs of ***E*** arising from 3H 1s AOs:

x-like ~ $(2\phi_2 - \phi_3 - \phi_4)/\sqrt{6}$

y-like ~ $(\phi_3 - \phi_4)/\sqrt{2}$

x-like ~ $a\mathrm{p}_{x1} + b(2\phi_2 - \phi_3 - \phi_4)/\sqrt{6}$ (σ MO)

~ $c\mathrm{p}_{x1} - d(2\phi_2 - \phi_3 - \phi_4)/\sqrt{6}$ (σ* MO)

y-like ~ $a\mathrm{p}_{y1} + b(\phi_3 - \phi_4)/\sqrt{2}$ (σ MO)

~ $c\mathrm{p}_{y1} - d(\phi_3 - \phi_4)/\sqrt{2}$ (σ* MO)

Further combination of ***E***-type MOs of two fragments gives extended MOs.