CH105
Fun of Organic and Inorganic Chemistry

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Instructor (Inorganic): Prof. C.P. Rao
(Starts in the Middle of August)

1

In *Teacher and Child*, noted psychologist Haim Ginott includes a copy of a letter that a principal sent to his teachers at the beginning of each new school year.

Dear Teacher,

I am a survivor of a concentration camp. My eyes saw what no man should witness:

- **Gas chambers built by learned engineers**
- **Children poisoned by educated physicians**
- **Infants killed by trained nurses**
- **Women and babies shot and burned by high school and college graduates**

So I am suspicious of education. My request is: Help your students become human. Your efforts must never produce learned monsters, skilled psychopaths, educated Eichmanns.

Reading, writing, arithmetic are important only if they serve to make our children more human.

2

Think on These Things

Can we work hard like an ambitious person, but not be ambitious ?

Can we put in our best in a game and be equally happy if our friend wins ?

Can we live without comparison, without feeling superior or inferior to anyone else ?

Can we love each other without psychologically leaning on each other, using each other ?

Is education meant only to cultivate certain abilities, use them in the outside world to gain maximum material advantages, accept all the greed, violence and corruption of society and contribute further to it ?

These are the questions we all must ask, both individually and also collectively.

http://www.pkrishna.org/What-Is-K-Education.html

3

4

Why One Should Learn Other Disciplines?

Question: You have often said, "Specialists are dangerous people".

Answer: Only specialists are dangerous, because they begin to construct the whole world in terms of their specialty, and in terms of the advances their specialty is supposed to have made irrespective of the relation it has with other aspects...... Wisdom does not come from a single discipline, this tendency of the world to break up into a large number of superspecialities is very dangerous. Mere experts, mere specialists are dangerous, but nonexperts are useless!

Prof. Yashpal

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(to Nat'l Science Teachers Assn. 1966)

Why quote Feynman?
~~Because he is an expert?~~

Scie...
the ignorance of experts.

When someone says science teaches such and such, he is using the word incorrectly. Science doesn't teach it; e...

Because what he says makes sense.

If they say to you science has shown such and such, you might... lid the scientists

Though literally "expert" *means* **someone who has done experiments.**

this o...

6

3

Experiments are indispensable in

organic chemistry

(an empirical science)

but so is logic

Believe what I say *only* when
it makes sense to you.

What if it doesn't?
Can we learn together?

Real Learning Requires Attendance and Attention

Attention is not the same thing as concentration. Concentration is exclusion; attention, which is total awareness, excludes nothing

– J.Krishnamurty
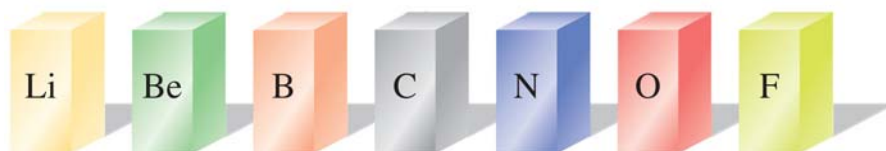**Freedom from the Known,31**

8

4

Organic Chemicals in Action

9

Top 200 Pharmaceutical Products by Worldwide Sales in 2008

What Makes Carbon So Special?

the second row of the periodic table

- **Atoms to the left of carbon give up electrons.**
- **Atoms to the right of carbon accept electrons.**
- **Carbon shares electrons.**

Outline

- **Huckel Theory For Conjugated Systems**

- **Stereochemistry**

- **Conformational Analysis**

- **Chemistry of Carbonyl Compounds**

  Total number of lectures: 7 (1.5 h x 7)

12

6

Tutorial Sessions

When: Wednesdays from 3-4 PM

Venue: Lecture Theater (LT) Rooms:

LT 301 (T1), LT 302 (T2), LT 303 (T3), LT 202 (T4), LT 203 (T5)

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Text Book

- **Organic Chemistry by Wade/Loudan/Bruice or Solomons**

  Don't Buy any Text Book (Relevant Chapters in PDF from Bruice's Book will be made available to you)

  Additional Reading

- **Organic Chemistry, Clayden, Green, Warren and Wothers, Oxford University Press**

  Animations
  http://www.chemtube3d.com/

  http://winter.group.shef.ac.uk/orbitron/

  http://symmetry.otterbein.edu/gallery/index.html

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Evaluation

Quiz1 (Final Exam)

25 marks for Organic +

Quiz 2 for 25 marks for ONLY
Inorganic

Date will be announced in the next
class

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Join the Facebook Group

CH_ORGANIC_IITB_2014

Announcements

Links to Relevant Podcasts

Animation Videos

More Think on These Things &

Online one-to-one interactions

Lecture Slides in Moodle IITB

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Help Session

Do you have

1. Issues in understanding English language, as used in the lectures?
2. Problems in understanding stereochemistry or difficulty in visualizing 3D structures?
3. Difficulty in understanding the contents of the lecture slides?
4. Are you shy in asking questions? Or have fear of being foolish in asking questions?
5. Do you hate organic chemistry?

Contact me by mail/phone at the earliest

Huckel Theory
For Conjugated Systems

Lecture slides are courtesy of : Prof. R.B Sunoj, IIT Bombay
Prof. Peter Volhardt, UC Berkeley
Prof. J. M McBride, Yale University
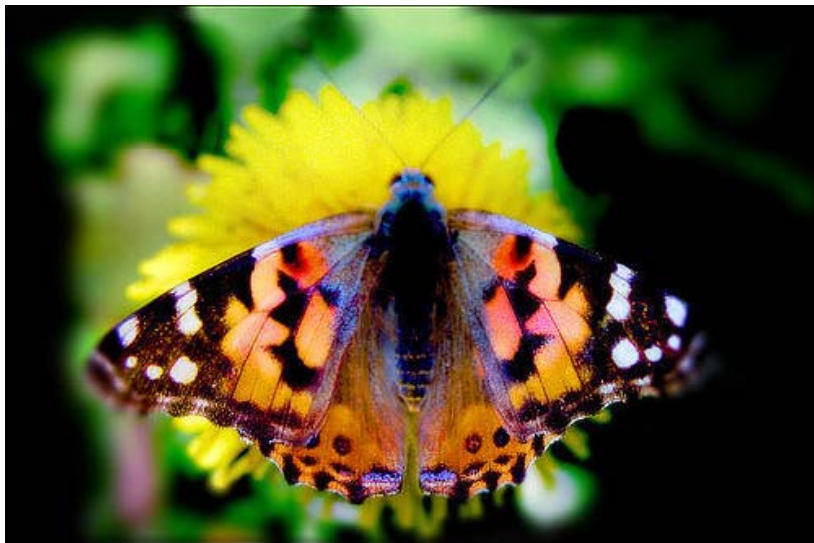Oxford University Press
Pearson Education

18

Symmetry of objects

19

Symmetry in Nature

20

Symmetry

Symmetry Elements

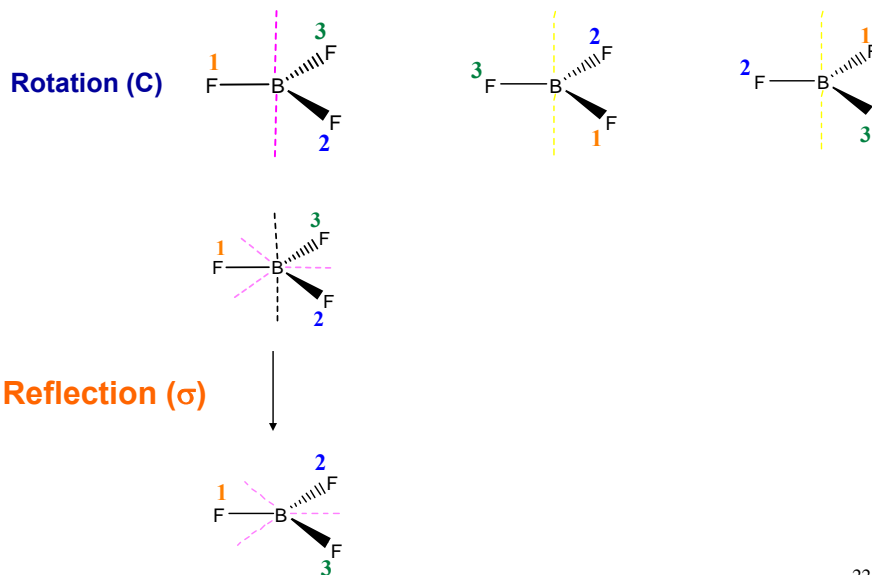**A geometrical entity such as** **a line****,** **a plane** **or** **a point****, with respect to which one or more symmetry operations may be carried out**

1. **Plane of symmetry (σ)**

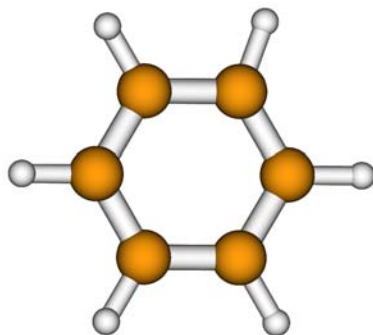2. **Center of symmetry or (inversion symmetry)-(i)**

3. **Axis of symmetry (C)**

21

Symmetry in Molecules

Rotation (C)

Reflection (σ)

22

http://symmetry.otterbein.edu/gallery/index.html

Molecular Symmetry

One C$_6$ axis, Six C$_2$ axes

One σ_h, Six σ_v

One *i*

http://symmetry.otterbein.edu/gallery/index.html 23

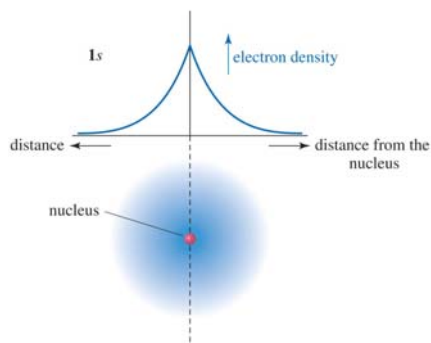
Electronic Structure of the Atom

- **An atom has a dense, positively charged nucleus surrounded by a cloud of electrons.**

- **The electron density is highest at the nucleus and drops off exponentially with increasing distance from the nucleus in any direction.**
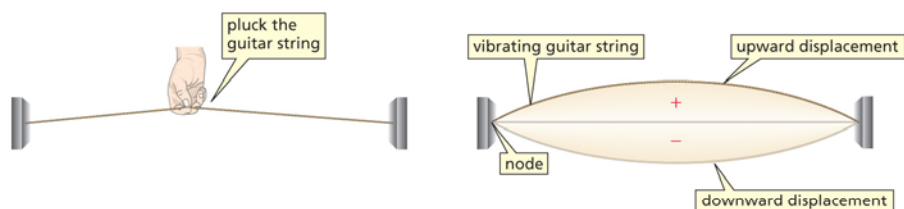

1s   electron density

distance ← → distance from the nucleus

nucleus

http://winter.group.shef.ac.uk/orbitron

Chapter 1   24

A Standing Wave

# Wave Properties of Electrons/Orbitals

- Standing wave vibrates in fixed location.
- Wave function, ψ, is a mathematical description of size, shape, and orientation.
- Amplitude may be positive or negative.
- *Node*: Amplitude is zero.

http://winter.group.shef.ac.uk/orbitron

Chapter 2

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The 2*p* Orbitals

- There are three 2*p* orbitals, oriented at right angles to each other.
- Each *p* orbital consists of two lobes.
- Each is labeled according to its orientation along the *x*, *y*, or *z* axis.

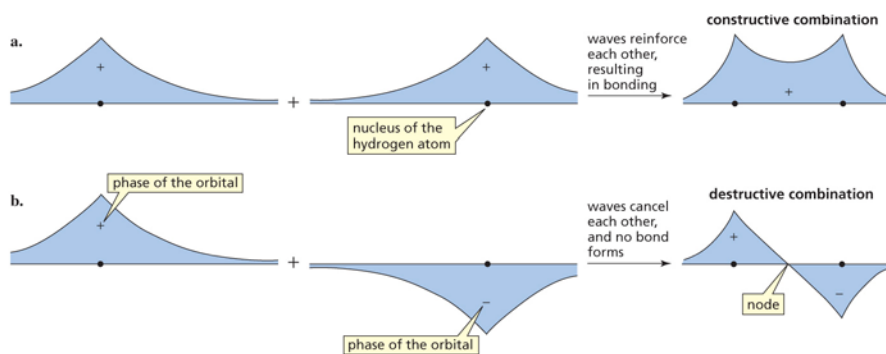**http://winter.group.shef.ac.uk/orbitron**
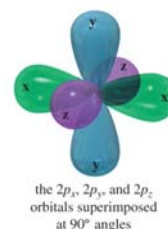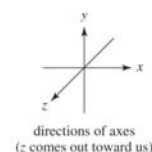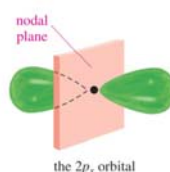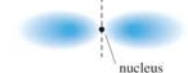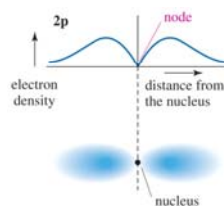
Linear Combination of Atomic Orbitals

- **Combining orbitals between two different atoms is *bond formation*.**

- **Combining orbitals on the same atom is *hybridization*.**

- **Conservation of orbitals**

- **Waves that are in phase add together. Amplitude increases.**

- **Waves that are out of phase cancel out.**

Waves Can Reinforce Each Other;
Waves Can Cancel Each Other

a. waves reinforce each other, resulting in bonding — constructive combination

nucleus of the hydrogen atom

phase of the orbital

b. waves cancel each other, and no bond forms — destructive combination

node

phase of the orbital

Orbital Symmetry

σ*

σ

Symmetric along the axis
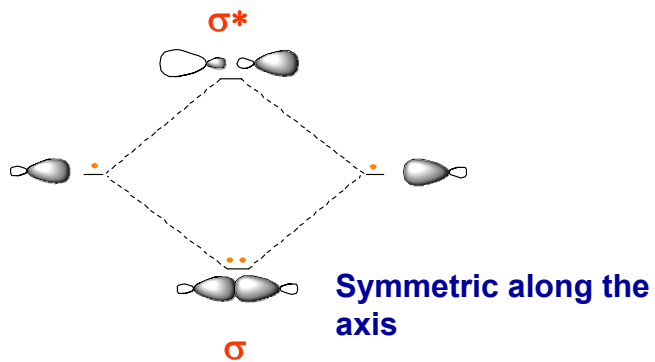
For any bonding molecular orbital (BMO) there should be a corresponding antibonding molecular orbital (ABMO)

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Ethylene MOs

Ethylene shows interesting properties due to the presence of a π-bond

The C-C π-orbital is the Highest Occupied Molecular Orbital (HOMO) of the alkene
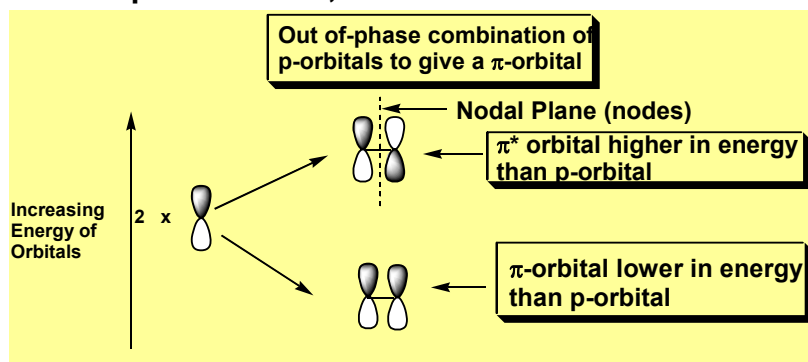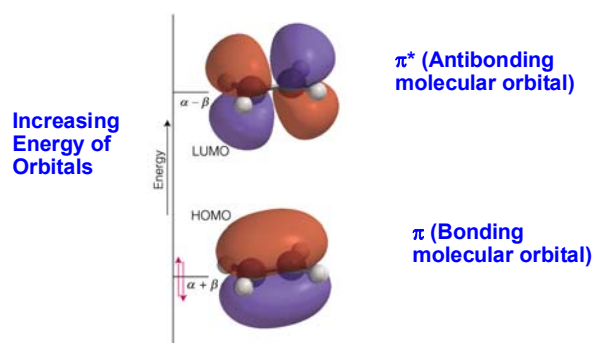
Linear Combination of p-orbitals, leading to C-C π-orbital can be represented as,

Out of-phase combination of p-orbitals to give a π-orbital

Nodal Plane (nodes)

π* orbital higher in energy than p-orbital

Increasing Energy of Orbitals

2 x

π-orbital lower in energy than p-orbital

Ethylene MOs

Increasing Energy of Orbitals

$\alpha - \beta$

LUMO

HOMO

$\alpha + \beta$

π* (Antibonding molecular orbital)

π (Bonding molecular orbital)

Total Number of π-electrons = 2
Total Number of π-orbitals = 2
Both electrons will occupy the lowest energy MO, i.e., BMO

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How about MOs for allyl system?

the p orbital has the correct symmetry to combine with
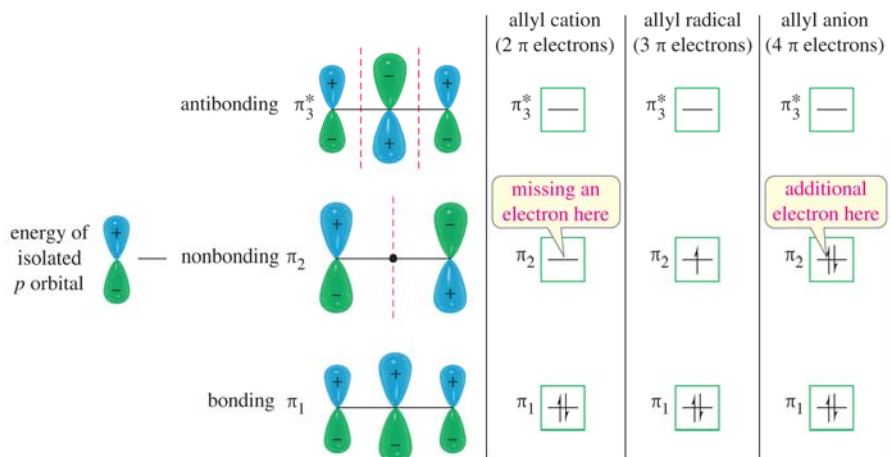the π bond to form a new molecular orbital for the allyl system
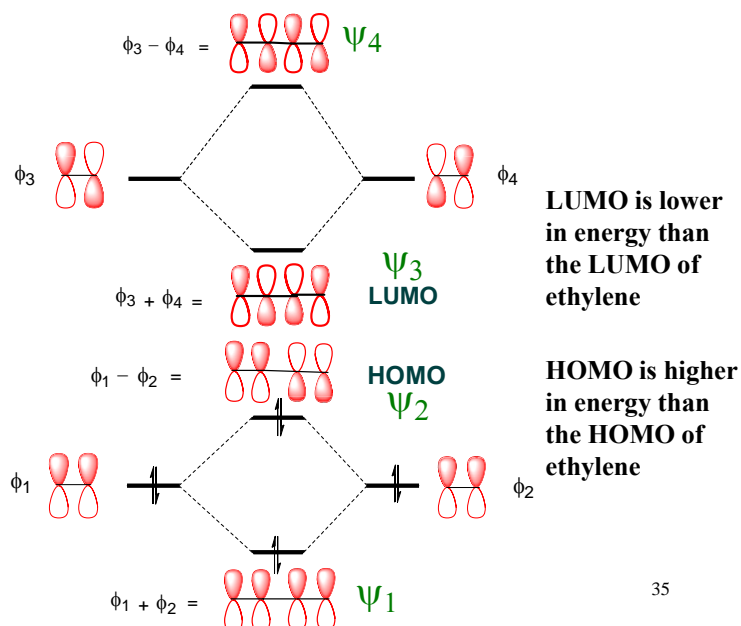
the bonding molecular
orbital of the allyl system, Ψ_1

nodal plane
through the middle atom
nonbonding Ψ_2

two nodal planes
antibonding Ψ_3
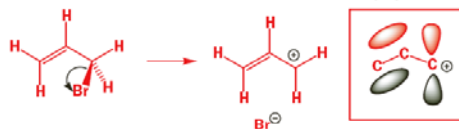
the π molecular orbitals of the allyl system: the allyl cation

increasing energy of orbitals

$3\times$

three degenerate
2p orbitals combine
to form three
molecular orbitals

combine

Ψ_3 — antibonding
molecular orbital
higher in energy
than a p orbital

Ψ_2 — nonbonding
molecular orbital
Same energy
as a p orbital — this is the
*Lowest Unoccupied
Molecular Orbital*
(LUMO)

Ψ_1 — bonding orbital.
energy lower
than p orbital — this is the
*Highest Occupied
Molecular Orbital*
(HOMO)

three molecular orbitals
resulting from the combinations
of the three atomic orbitals
the energies are now different

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MOs for the Allylic Species

energy of
isolated
p orbital

antibonding π_3^*

nonbonding π_2

bonding π_1

	allyl cation (2 π electrons)	allyl radical (3 π electrons)	allyl anion (4 π electrons)
π_3^*	—	—	—
π_2	missing an electron here	+	additional electron here ⇅
π_1	⇅	⇅	⇅

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Can we construct butadiene MOs?

$\phi_3 - \phi_4 =$ ψ_4

ϕ_3 ϕ_4

$\phi_3 + \phi_4 =$ ψ_3 **LUMO**

$\phi_1 - \phi_2 =$ **HOMO** ψ_2

ϕ_1 ϕ_2

$\phi_1 + \phi_2 =$ ψ_1

LUMO is lower in energy than the LUMO of ethylene

HOMO is higher in energy than the HOMO of ethylene

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Butadiene MOs

Total number of $p\pi$-orbitals = 4

Total number of π-electrons = 4

3   2

4   1

combine out-of-phase ψ_4

combine in-phase ψ_3 LUMO

Increasing energy of orbitals

α

combine out-of-phase ψ_2 HOMO
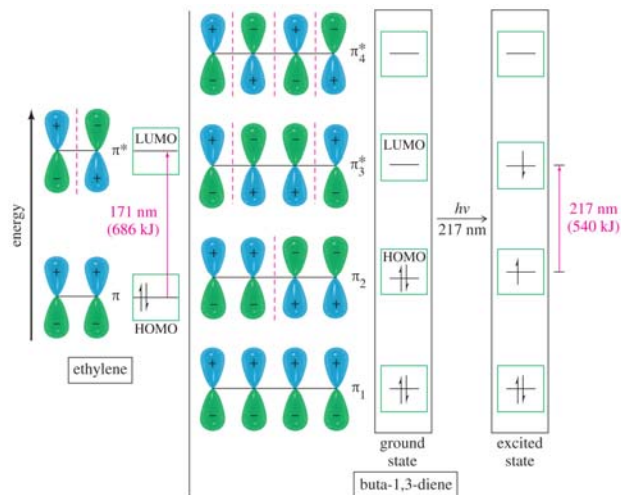
combine in-phase ψ_1
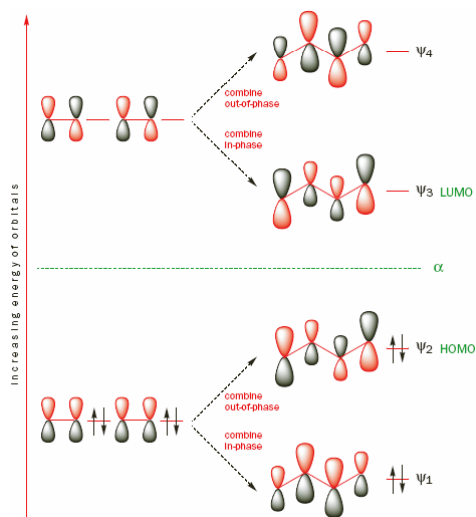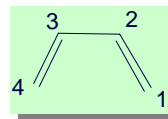
Butadiene is more reactive than ethylene
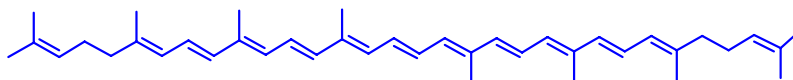
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HOMO-LUMO Gap

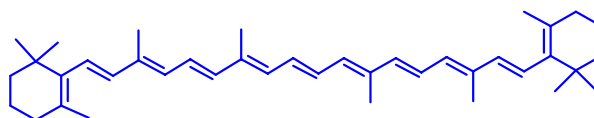# $\pi \to \pi^*$ for Ethylene and Butadiene

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Extended Conjugation and Colour (E.g. 1)

If the conjugation is extended further, the gap between HOMO and LUMO will decrease to allow the compound to absorb visible light and hence be COLOURED.
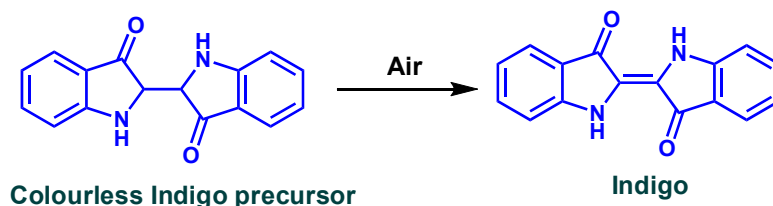

Lycopene, the red pigment present in tomatoes and other berries

β-carotene, the red pigment present in carrots and other vegetables

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Extended Conjugation and Color (E.g. 2)

The colour of the blue jeans come from the pigment indigo

Colourless Indigo precursor

Indigo

Jeans are generally dyed by immersion in a vat of reduced indigo, which is colourless since there is no conjugation.

When the cloth is hung up to dry, the oxygen in the air oxidizes the pigment to indigo and the jeans turn blue.

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Generalizations for Acylic Polyenes

The lowest energy orbital is always symmetric with respect to the principal mirror plane

The number of nodes increases by ONE on going from one orbital to the next higher energy orbital

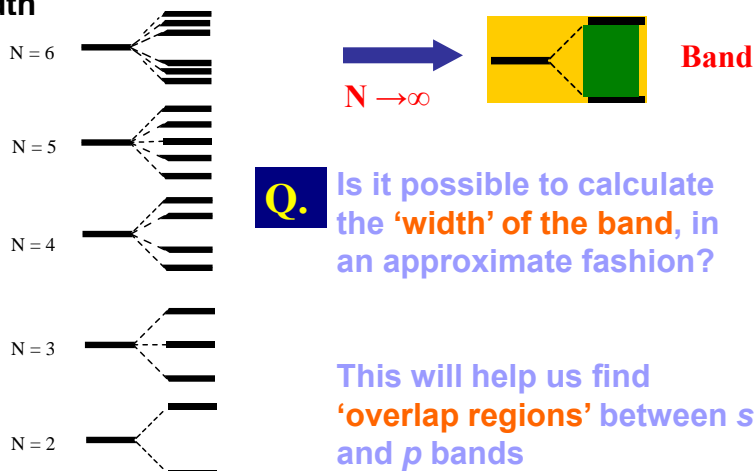**Nodes must be symmetrically located with respect to the central mirror plane**

In systems with an odd number of atoms, the antisymmetric levels can have node/nodes at the carbon atoms. (homework: penta dienyl cation)

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Polyenes to Solids

When Number of atoms (N) in a polyene become infinitely large, the difference between neighboring energy levels (MO-levels) is infinitely small. But the band has a finite width

N = 6

N = 5

N = 4

N = 3

N = 2

$N \rightarrow \infty$

Band

Q. Is it possible to calculate the 'width' of the band, in an approximate fashion?

This will help us find 'overlap regions' between *s* and *p* bands

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Polyenes-to-Solids Analogies

Approximate Analogs Between Molecular and Solid-State Terminologies
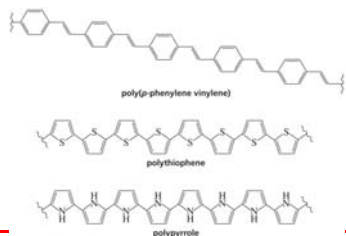
Molecular Orbital	Band Orbital
HOMO	Valence Band
LUMO	Conduction Band
HOMO-LUMO gap	Band gap

poly(p-phenylene vinylene)

polythiophene

polypyrrole

Advanced and Related Topics: Organic Semiconductors, Organic LEDs, Conducting Polymers

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Some questions of significance

Most of the reactivities of conjugated systems (say, butadiene, or a carbonyl compound) primarily arise due to the π-molecular orbitals.

**Is it possible to estimate the energies of the π-molecular orbitals?**

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Huckel MO Theory

Basic Approximations

- **Used for the treatment of conjugated systems**

- **The π-system is treated independently of the σ-framework in planar conjugated molecules**

- **Or π-system <u>do not interact</u> with the σ-skeleton**

- **Interactions between pπ orbitals located on atoms which are <u>not directly linked</u> is zero**

π-electron approximation: π-electrons move in some fixed effective potential of σ framework

pi-system

Sigma-Framework

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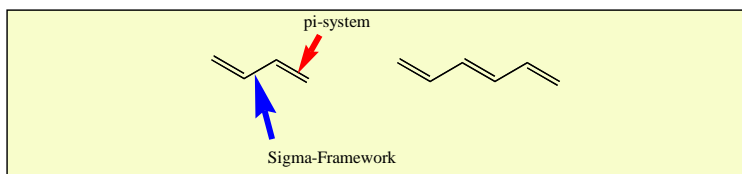
Energies of MOs in terms of Integrals

The energy of each pπ-orbital before interaction is set equal to α, (Coulomb integral)

[*refers to energy of an electron in the field of its own nucleus*]
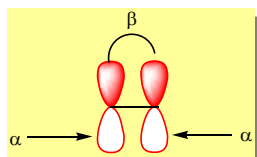
[*can be taken as valence state ionization potential*]

?

The interaction energy between two adjacent *pπ* orbitals equals to β (Resonance integral)

[*refers to energy of i ^th electron in the field of j ^th nucleus*]

[*can be taken as the interaction between atomic orbitals i and j*]

[energy of an electron in the field of two or more nuclei]

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Energies of MOs

The energy of the *j*^th MO for a linear unbranched conjugated polyene with *N* pπ orbitals (or N number of carbon atoms) is given by

$$e_j = \alpha + 2\beta Cos\frac{\pi}{N+1}j$$

The energy of the *j*^th MO for a cyclic polyene with *N* pπ orbitals is given by

$$e_j = \alpha + 2\beta Cos\frac{2\pi}{N}j$$

j = 0, 1, 2,..N-1

Note: α and β are negative (attractive !) by definition

The α and β are not calculated as numerical values, but the energies are expressed in terms of these quantities

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Energies of MOs

For ethylene   **Linear polyenes**

Energy of LUMO = $\alpha - \beta$

Energy of HOMO = $\alpha + \beta$

For Butadiene

Energy of LUMO = $\alpha - 0.62\beta$

Energy of HOMO = $\alpha + 0.62\beta$

Linear polyenes

When the number of orbitals in the chain increases, the energies will be as,

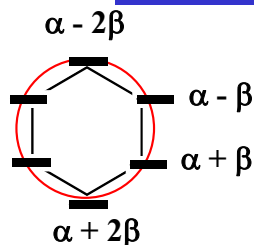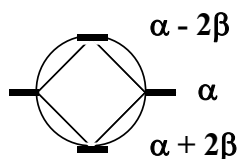**For   Highest energy MO = $\alpha - 2\beta$**

Lowest energy MO = $\alpha + 2\beta$

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Energies of MOs

Cyclic polyenes

Draw a circle of radius 2β and inscribe an N-vertex polygon such that two vertices are in the six o'clock position. The points of contact between the circle and the polygon defines the energy levels   **Frost Diagram**

$\alpha - 2\beta$

$\alpha - 2\beta$

α

$\alpha + 2\beta$

$\alpha - \beta$

$\alpha + \beta$

$\alpha + 2\beta$

The energy level α is at the same level as that of the center of the circle

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Energies of MOs

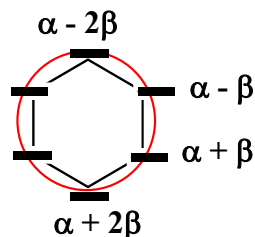**Calculate the total energy of π-electrons in benzene?**

Total number of π-electrons = 6

Total energy

$$= 2 * (\alpha + 2\beta) +$$

$$4 * (\alpha + \beta)$$

$$\overline{\qquad\qquad}$$

$$6\alpha + 8\beta$$

$\alpha - 2\beta$

$\alpha - \beta$

$\alpha + \beta$

$\alpha + 2\beta$

If the double bonds were localized (not conjugated)!
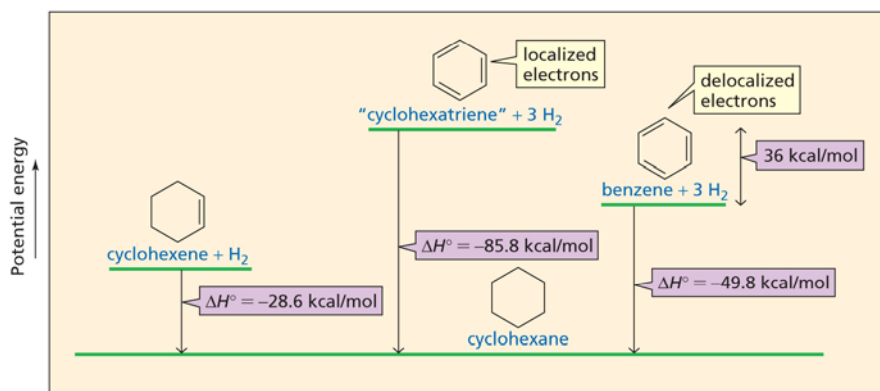
Equivalent to three ethylenes

Total energy $\qquad = 6 * (\alpha + \beta)$

Additional Stabilization in Benzene (fully delocalized) = 2β

[What is the resonance stabilization energy in benzene?]

Benzene is unusually unreactive. Does this mean that it is also especially stable thermodynamically? Look at $\Delta H°$ hydrogenation:

Potential energy

localized electrons

"cyclohexatriene" + 3 H_2

delocalized electrons

36 kcal/mol

benzene + 3 H_2

cyclohexene + H_2

$\Delta H° = -85.8$ kcal/mol

$\Delta H° = -28.6$ kcal/mol

$\Delta H° = -49.8$ kcal/mol

cyclohexane

Special stability is now called aromaticity. All cyclic 6e arrangements are aromatic, including transition states.

π Molecular Orbitals of Benzene
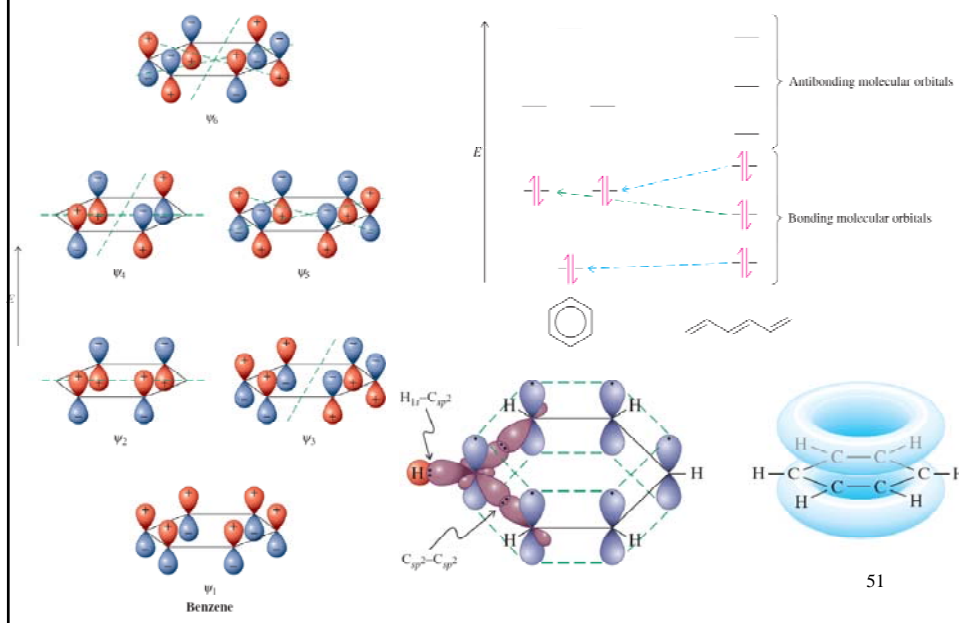
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Huckel's Rule of Aromaticity

• **Planar, fully conjugated, monocyclic systems with $\underline{(4n+2)\pi}$ electrons** **having a closed shell of electrons all in bonding orbitals** **are exceptionally stable. Such compounds are said to be <u>aromatic</u>**

• **Analogous systems with $\underline{4n\ \pi}$ <u>electrons</u> are described as** **anti-aromatic**

i

Modern definition of aromaticity:

Compounds that possesses the ability to sustain induced ring current when subjected to magnetic field

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Additional Informations

https://moodle.iitb.ac.in/

- **Lecture Slides on Molecualr Orbitals and Aromaticity**

- **Relevant materials from Books (check the book chapter folder)**

- **Basic and very good book to read : Organic Chemistry by Solomons**

- **Promote cooperative learning: make a group of 5-10 and discuss together at least twice in a week**

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Huckel's Rule and Aromaticity

The compound must have an uninterrupted cyclic π-cloud of electrons

For the π-cloud to be cyclic, the molecule must be cyclic.

For the π-cloud to be uninterrupted, every atom in the ring must have a p-orbital

For the π-cloud to form, each p-orbital must be able to overlap with the p-orbitals on either side of it. This means that the molecule must be planar.

E.g., 1
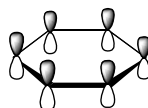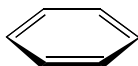
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Huckel's Rule and Aromaticity
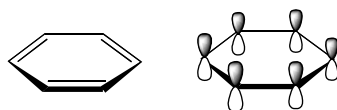
- **It must have an uninterrupted cloud of π electrons.**

  (cyclic, planar, every ring atom must have a p orbital).

- **The π cloud must have an odd number of pairs of π electrons.**
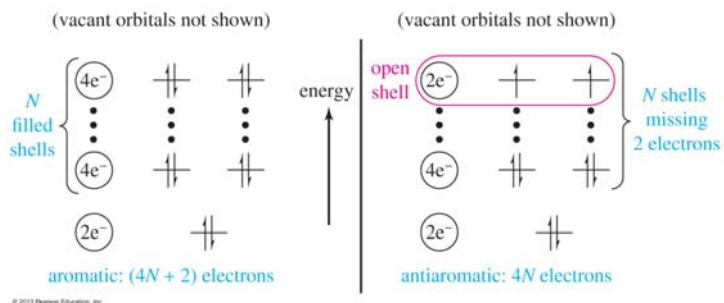
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Huckel's Rule of Aromaticity
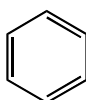
Number of π electrons = 6

Satisfies Huckel' rule, where n = 1

Aromatic
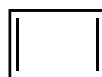
Number of π electrons = 4

Where n = 1

Anti-aromatic

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MO Derivation of Hückel's Rule

(vacant orbitals not shown)   (vacant orbitals not shown)

- **Aromatic compounds have (4N + 2) electrons and the orbitals are filled.**

- **Antiaromatic compounds have only 4N electrons and have unpaired electrons in two degenerate orbitals.**

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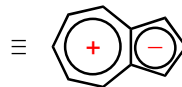
Examples for Aromatic Compounds
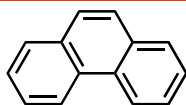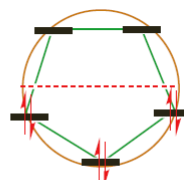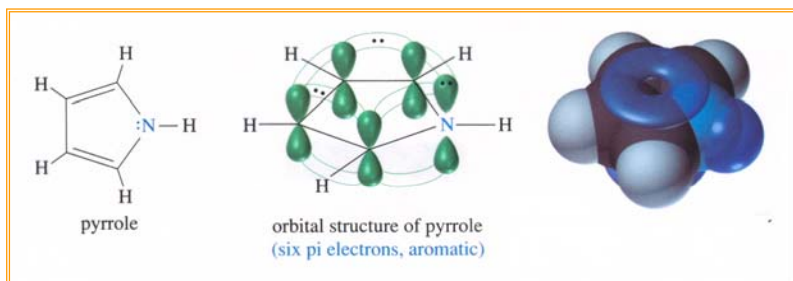

Phenathrene   **cyclopentadienyl anion**
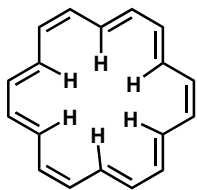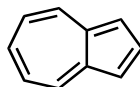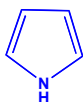
[18]-annulene   **Azulene**

deprotonation of cyclopentadiene gives
the stable cyclopentadienyl anion

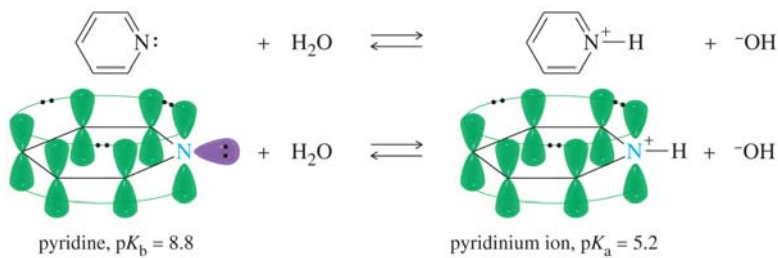the anion has 6π electrons
completely filling the bonding MOs

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Aromatic Heterocyclic Compounds
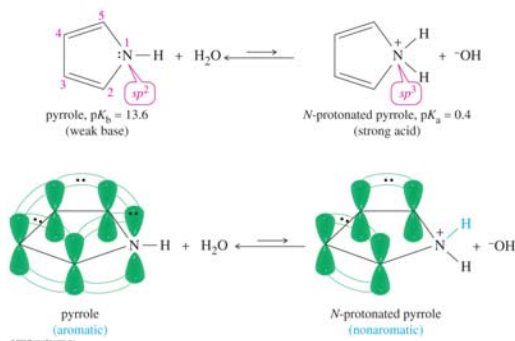
Lone pair is part of the aromatic system

pyrrole

orbital structure of pyrrole
(six pi electrons, aromatic)

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Pyridine is a Base

pyridine, pK_b = 8.8
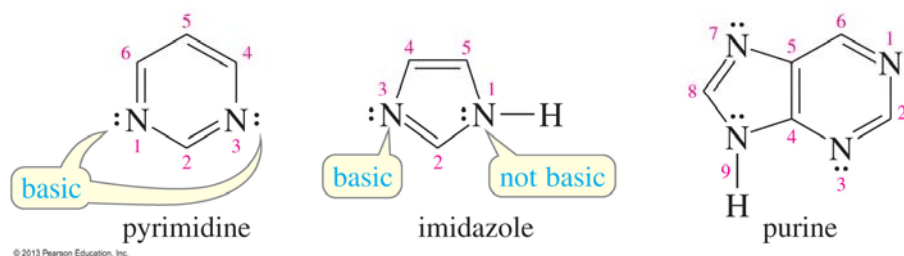
pyridinium ion, pK_a = 5.2

- **Pyridine is basic, with a pair of nonbonding electrons available to abstract a proton.**

- **The protonated pyridine (the pyridinium ion) is still aromatic.**

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Pyrrole is a weak base

- **Pyrrole is aromatic because the lone pair on nitrogen is delocalized.**

- ***N*-protonated pyrrole is nonaromatic because the nitrogen is *sp³*.**
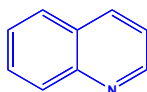
Basic or Nonbasic?

- **Pyrimidine has two basic nitrogens.**
- **Imidazole has one basic nitrogen and one nonbasic.**
- **Only one of purine's nitrogens is not basic.**
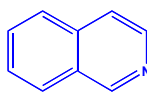
Aromatic Heterocyclic Compounds
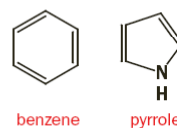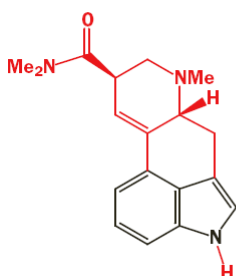
Lone pair not involved in aromatic system
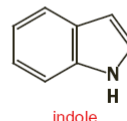
6π electrons   10π electrons

4n + 2 = 6, with n=1
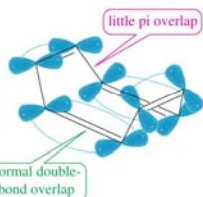
benzene   pyrrole

indole

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Examples of Antiaromatic Compounds

Cyclic planar molecules with conjugated 4n π-electrons (where n is an integer) are antiaromatic

Antiaromatic compounds are less stable than the open chain counterpart

little pi overlap

eight pi electrons

normal double-bond overlap

A cyclic compound that does not have a continuous conjugated p orbitals are known as <u>nonaromatic</u>

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e.g., 1,3,5-cycloheptatriene

"The mind is a superb instrument if used rightly. Used wrongly, however, it becomes very destructive. To put it more accurately, it is not so much that you use your mind wrongly - you usually don't use it at all. **It uses you. This is the disease.** You believe that you are your mind. This is the delusion. The instrument has taken you over."

Eckhart Tolle: The Power of Now

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The Secular Determinant

Start with a trial wave function

$$\phi = c_1 f_1 + c_2 f_2 \quad\text{---}(1)$$

Solve variational integral,

$$\frac{\langle \phi | \hat{H} | \phi \rangle}{\langle \phi | \phi \rangle} = E\phi \quad\text{---}(2)$$

$$\int \phi^* \hat{H} \phi \, d\tau = \int (c_1 f_1 + c_2 f_2) \hat{H} (c_1 f_1 + c_2 f_2) \, d\tau$$

$$= c_1^2 \hat{H}_{11} + 2 c_1 c_2 \hat{H}_{12} + c_2^2 H_{22} \quad\text{---}(3)$$

where $\int f_i \hat{H} f_j = \hat{H}_{ij}$ and $H_{ij} = H_{ji}$

$$\int \phi^* \phi \, d\tau = c_1^2 S_{11} + 2 c_1 c_2 S_{12} + c_2^2 S_{22} \quad\text{---}(4)$$

where $\int f_i f_j = S_{ij}$ and $S_{ij} = S_{ji}$

Minimizing energy E with respect c_1 and c_2

$$E(c_1, c_2) = \frac{c_1^2 \hat{H}_{11} + 2c_1 c_2 \hat{H}_{12} + c_2^2 H_{22}}{c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22}}$$

$$c_1^2 \hat{H}_{11} + 2c_1 c_2 \hat{H}_{12} + c_2^2 \hat{H}_{22} = E(c_1^2 S_{11} + 2c_1 c_2 S_{12} + c_2^2 S_{22})$$
$$\text{——(5)}$$

Maximum contribution from f_1 to the total function ϕ will happen if

$$\frac{\partial E}{\partial c_1} = 0$$

Differentiate (5) with respect to c_1

$$c_1 \hat{H}_{11} + c_2 \hat{H}_{12} = E(c_1 S_{11} + c_2 S_{12})$$

$$(H_{11} - E S_{11})c_1 + (H_{12} - E S_{12})c_2 = 0$$

Similary, differentiating w.r.t c_2

$$(\; \;)c_1 + (H_{22} - E S_{22})c_2 = 0$$

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Two linear simultaneous equations in c_1 and c_2 can exist only if the following determinant is equal to zero,

ie

$$\begin{vmatrix} H_{11} - E S_{11} & H_{12} - E S_{12} \\ H_{21} - E S_{21} & H_{22} - E S_{22} \end{vmatrix} = 0 \quad \text{——(6)}$$

Secular Determinant

Substituting $\boxed{\begin{aligned} H_{ii} &= \alpha \\ H_{ij} &= \beta \end{aligned}}$

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