


### Electron structure of molecules, chemical bonding

**Classical bonding theories: valence and electron theory**

- Experience can be interpreted readily.

#### Lewis theory

- **Valence electron:** decisive role in the formation of various chemical bonds.
- Electron transfer → ionic bond,
- electron sharing → covalent bond.
- Atoms tend to achieve noble gas electron configuration – *octet rule.*



Gilbert Newton Lewis (1875 -1946)

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#### Lewis structures

- A symbol stands for the atom and the core electrons.
- Dots represent *valence electrons.*

$$\text{Na} \cdot + \cdot \ddot{\text{Cl}} : \rightarrow \text{Na}^+ + : \ddot{\text{Cl}} :^-$$

$$: \ddot{\text{Cl}} : + \cdot \ddot{\text{Cl}} : \rightarrow \begin{matrix} \text{Cl} & \text{Cl} \\ \vdots & \vdots \\ \text{Cl} & \text{Cl} \end{matrix} \text{ or } \begin{matrix} | & | \\ \text{Cl} & \text{Cl} \\ | & | \end{matrix}$$

Bonding electron pairs  
Lone electron pairs

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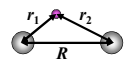
**Quantum mechanics:**

- Molecules are quantum mechanical systems consisting atoms and electrons,
- their possible energy states can be determined from the stationary Schrödinger equation.
- Molecules and molecular ions can be interpreted by the same method.
- The full description involves the movements of nuclei,
- when the electron energies are calculated, the nuclei are assumed to be stationary (Born-Oppenheimer approximation).
- The stationary Schrödinger equations of multi-electron systems cannot be solved precisely (analytically).

**Quantum chemistry:**

- Finding approximation methods,
- executing computations,
- chemical interpretations of results.

### Electron structure of molecules, the hydrogen molecule ion (H<sub>2</sub><sup>+</sup>)



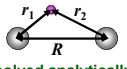
- The simplest possible quantum chemical system that features a chemical bond.
- A single particle to be described ( $\psi$ ) in the Born-Oppenheimer approximation.
- Stationary Schrödinger equation:

$$\left[ -\frac{\hbar^2}{2\mu} \Delta + \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{R} - \frac{1}{r_1} - \frac{1}{r_2} \right) \right] \Psi = E\Psi \text{ and } \Psi = \varphi\sigma$$

Spatial wave function    Spin function

$$\left[ -\frac{\hbar^2}{2\mu} \Delta + \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{R} - \frac{1}{r_1} - \frac{1}{r_2} \right) \right] \varphi = E\varphi$$

### Electron structure of molecules, the hydrogen molecule ion (H<sub>2</sub><sup>+</sup>)




- It can be solved analytically.
- **It is easier to solve with an approximation based on variation:**
- The probe function for the ground state can be constructed by the linear combination of the 1s orbitals of the two nuclei (LCAO: Linear Combination of Atomic Orbitals):

$$\varphi = c_1\varphi_1 + c_2\varphi_2$$

Real coefficients

$$\left[ -\frac{\hbar^2}{2\mu} \Delta + \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{R} - \frac{1}{r_1} - \frac{1}{r_2} \right) \right] \varphi = E\varphi \text{ or } H\varphi = E\varphi$$

### Electron structure of molecules, the hydrogen molecule ion (H<sub>2</sub><sup>+</sup>)



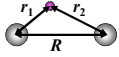
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$$\varphi = c_1\varphi_1 + c_2\varphi_2 \quad H_{ij} = \int \varphi_i^* H \varphi_j dV$$

$$E = \frac{\int \varphi^* H \varphi dV}{\int \varphi^* \varphi dV} \quad S_{ij} = \int \varphi_i^* \varphi_j dV$$

$$E = \frac{H_{11}c_1^2 + H_{12}c_1c_2 + H_{21}c_2c_1 + H_{22}c_2^2}{S_{11}c_1^2 + S_{12}c_1c_2 + S_{21}c_2c_1 + S_{22}c_2^2}$$

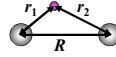
### Electron structure of molecules, the hydrogen molecule ion ( $H_2^+$ )



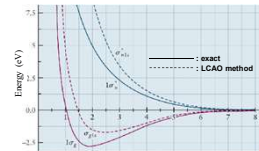
- It can be solved analytically.
- **It is easier to solve with an approximation based on variation:**
- The probe function for the ground state can be constructed by the linear combination of the 1s orbitals of the two nuclei (LCAO: Linear Combination of Atomic Orbitals):
- As 1s orbitals are normalized  $S_{11} = S_{22} = 1$ ,
- because of symmetry  $H_{11} = H_{22}$ ,  $H_{12} = H_{21}$
- additionally  $S_{12} = S_{21} = S$
- Possible values of energy:

$$E_g = \frac{H_{11} + H_{12}}{1 + S} \quad E_u = \frac{H_{11} - H_{12}}{1 - S}$$

### Electron structure of molecules, the hydrogen molecule ion ( $H_2^+$ )



- Energy values are functions of internuclear distance  $R$ .
- A plot of these gives the energy-distance diagram of the  $H_2^+$  molecule ion:

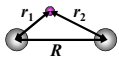


The electron on the  $\phi_u$  orbital has no minimum as a function of distance  $\rightarrow$  no chemical bond is formed (antibonding orbital)

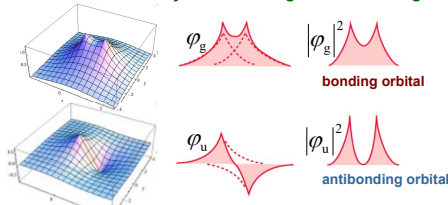
$\phi_g$  bonding orbital

	exact	LCAO
Equilibrium distance /pm	106	132
Dissociation energy /eV	2.79	1.78

### Electron structure of molecules, the hydrogen molecule ion ( $H_2^+$ )



- Energy values are functions of internuclear distance  $R$ .
- A plot of these gives the energy-distance diagram of the  $H_2^+$  molecule ion and the electron density of the bonding and antibonding orbitals:



### Electron structure of molecules, the molecular orbital (MO) method

- The stationary Schrödinger equation of a system containing  $M$  nuclei and  $N$  electrons:

$$\left[ -\frac{\hbar^2}{2\mu} \sum_{i=1}^N \Delta_i + \frac{e^2}{4\pi\epsilon_0} \left( -\sum_{i=1}^N \sum_{j=1}^M \frac{Z_j}{r_{ij}} + \sum_{i=1}^N \sum_{j=1}^N \frac{1}{r_{ij}} + \sum_{i=1}^M \sum_{j=1}^M \frac{Z_i Z_j}{R_{ij}} \right) \right] \Psi = E\Psi$$

distance of electron  $i$  from nucleus  $j$ 
distance between electrons  $i$  and  $j$ 
distance between nuclei  $i$  and  $j$

- This is solved by the independent particle approximation  $\rightarrow$  MO method
- The full multi-electron wave function of the molecule is constructed from the single electron wave functions (molecular orbitals) that extend to the entire molecule.
- The electron-electron interactions is taken into account as an average.
- Pauli' exclusion principle: a maximum of 2 electrons can reside on a single molecular orbital, they have different spin functions.

### Electron structure of molecules, the molecular orbital (MO) method



Robert Sanderson Mulliken (1897-1986)



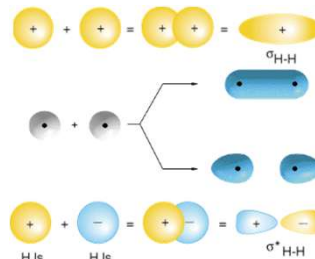
Friedrich Hund (1896-1997)

The molecular orbitals giving a good approximation for the full energy of the molecule can be found by the [Hartree-Fock method](#).

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### Electron structure of molecules, molecular orbitals of diatomic molecules

- Increase in electron density between nuclei: binding orbitals ( $\sigma_g, \pi_u, \delta_g$ )
- Decrease: antibonding orbitals\* ( $\sigma_u, \pi_g, \delta_u$ )



### Electron structure of molecules, molecular orbitals of diatomic molecules

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### Electron structure of molecules, molecular orbitals of diatomic molecules

- Increase in electron density between nuclei: **binding orbitals** ( $\sigma_g, \pi_u, \delta_g$ )
- Decrease: **antibonding orbitals\*** ( $\sigma_u, \pi_g, \delta_u$ )
- Molecular orbitals are constructed from the corresponding pairs of atomic orbitals.
- Energy series of the molecular orbitals (spectroscopic observations)

$$1\sigma_g < 1\sigma_u < 2\sigma_g < 2\sigma_u < 3\sigma_g < 1\pi_u < 1\pi_g < 3\sigma_u$$

The ordinal number of the orbital within its type.

- $\sigma_g$  and  $\sigma_u$  orbitals accommodate 2-2 electrons of opposite spins,
- $\pi_g$  and  $\pi_u$  orbitals host 4-4 electrons.
- The electron configuration can be given using the principle of energy minimum.

### Electron structure of molecules, molecular orbitals of homonuclear diatomic molecules

particle	electrons	configuration	bond order
H <sub>2</sub> <sup>+</sup>	1	1σ <sub>g</sub> <sup>1</sup>	1/2
H <sub>2</sub>	2	1σ <sub>g</sub> <sup>2</sup>	1
He <sub>2</sub> <sup>+</sup>	3	1σ <sub>g</sub> <sup>2</sup> 1σ <sub>u</sub> <sup>1</sup>	1/2
He <sub>2</sub>	4	1σ <sub>g</sub> <sup>2</sup> 1σ <sub>u</sub> <sup>2</sup>	0
Li <sub>2</sub>	6	[He <sub>2</sub> ]2σ <sub>g</sub> <sup>2</sup> 2σ <sub>u</sub> <sup>2</sup>	1
Be <sub>2</sub>	8	[He <sub>2</sub> ]2σ <sub>g</sub> <sup>2</sup> 2σ <sub>u</sub> <sup>2</sup>	0
B <sub>2</sub>	10	[Be <sub>2</sub> ]1π <sub>u</sub> <sup>4</sup>	1
C <sub>2</sub>	12	[Be <sub>2</sub> ]1π <sub>u</sub> <sup>4</sup>	2
N <sub>2</sub>	14	[Be <sub>2</sub> ]1π <sub>u</sub> <sup>4</sup> 3σ <sub>g</sub> <sup>2</sup>	3
O <sub>2</sub>	16	[N <sub>2</sub> ]1π <sub>g</sub> <sup>2</sup>	2
F <sub>2</sub>	18	[N <sub>2</sub> ]1π <sub>g</sub> <sup>4</sup>	1
Ne <sub>2</sub>	20	[N <sub>2</sub> ]1π <sub>g</sub> <sup>4</sup> 3σ <sub>g</sub> <sup>2</sup>	0

The difference between the number of electrons on bonding and antibonding orbitals.

- $\sigma_g$  and  $\sigma_u$  orbitals accommodate 2-2 electrons of opposite spins,
- $\pi_g$  and  $\pi_u$  orbitals host 4-4 electrons.
- The electron configuration can be given using the principle of energy minimum.

### Electron structure of molecules, molecular orbitals of homonuclear diatomic molecules

particle	electrons	configuration	bond order	D <sub>0</sub> /eV
H <sub>2</sub> <sup>+</sup>	1	1σ <sub>g</sub> <sup>1</sup>	1/2	2.793
H <sub>2</sub>	2	1σ <sub>g</sub> <sup>2</sup>	1	4.748
He <sub>2</sub> <sup>+</sup>	3	1σ <sub>g</sub> <sup>2</sup> 1σ <sub>u</sub> <sup>1</sup>	1/2	2.5
He <sub>2</sub>	4	1σ <sub>g</sub> <sup>2</sup> 1σ <sub>u</sub> <sup>2</sup>	0	-
Li <sub>2</sub>	6	[He <sub>2</sub> ]2σ <sub>g</sub> <sup>2</sup> 2σ <sub>u</sub> <sup>2</sup>	1	1.14
Be <sub>2</sub>	8	[He <sub>2</sub> ]2σ <sub>g</sub> <sup>2</sup> 2σ <sub>u</sub> <sup>2</sup>	0	-
B <sub>2</sub>	10	[Be <sub>2</sub> ]1π <sub>u</sub> <sup>4</sup>	1	3.0
C <sub>2</sub>	12	[Be <sub>2</sub> ]1π <sub>u</sub> <sup>4</sup>	2	6.36
N <sub>2</sub>	14	[Be <sub>2</sub> ]1π <sub>u</sub> <sup>4</sup> 3σ <sub>g</sub> <sup>2</sup>	3	9.902
O <sub>2</sub>	16	[N <sub>2</sub> ]1π <sub>g</sub> <sup>2</sup>	2	5.213
F <sub>2</sub>	18	[N <sub>2</sub> ]1π <sub>g</sub> <sup>4</sup>	1	1.34
Ne <sub>2</sub>	20	[N <sub>2</sub> ]1π <sub>g</sub> <sup>4</sup> 3σ <sub>g</sub> <sup>2</sup>	0	-

- The dissociation energy (D<sub>0</sub>) is proportional to the bond order:
  - a bond order of 0 means an unstable molecule (ion).
  - A molecule with a higher bond order has a higher D<sub>0</sub>.
- The Hartree-Fock method typically gives good approximations.
- The quality of the results depends on the base used.
- The electron cloud is asymmetric in heteronuclear molecules, one part of the molecule may be more positive or negative than the other → a polar bond is formed.

### Electron structure of molecules, molecular orbitals of heteronuclear diatomic molecules

Nonbonding orbitals form a bridge between classical chemical bonding theories and quantum mechanics.

Ground state molecules:  $1\sigma^2 2\sigma^2 3\sigma^2 4\sigma^2 1\pi^4 5\sigma^2$

Base (atomic orbitals):  $1s, 2s, 2p$  (carbon atom) and  $1s, 2s, 2p$  (oxygen atom)

Nonbonding orbitals

### Electron structure of molecules, molecular orbitals of heteronuclear diatomic molecules

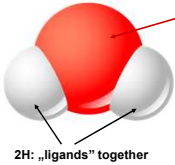
Nonbonding orbitals form a bridge between classical chemical bonding theories and quantum mechanics.

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- The quality of the results depends on the base used.
- The electron cloud is asymmetric in heteronuclear molecules, one part of the molecule may be more positive or negative than the other → a polar bond is formed.

Molecule	r /pm		D <sub>0</sub> /eV	
	computed (HF)	measured	computed (HF)	measured
CO	100.18	112.82	7.89	11.24
LiF	152.83	156.37	4.03	5.987
HF	89.75	91.65	4.38	6.12

### Electron structure of molecules, molecular orbitals of polyatomic molecules

- The construction of the molecular orbitals with the proper symmetry from atomic orbitals is non-trivial.
- Group theory gives some guidelines that can be used readily.



O: central atom

2H: „ligands” together

- The 1s orbitals of the **hydrogen atoms** are used to create orbital groups.
- In the  $C_{2v}$  point group, this base is in the following reducible representation:

$C_{2v}$	$E$	$C_2$	$\sigma_v(xy)$	$\sigma_v(yz)$
$\Gamma$	2	0	2	0

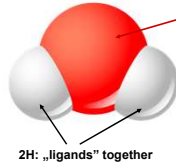
- Reduction gives  $\Gamma = A_1 + B_1$ ;

$$\chi_1 = \frac{1s_{H1} + 1s_{H2}}{\sqrt{2}} \quad \text{és} \quad \chi_2 = \frac{1s_{H1} - 1s_{H2}}{\sqrt{2}}$$

- The symmetry of the atomic orbitals of **oxygen** are found directly in the table.

### Electron structure of molecules, molecular orbitals of polyatomic molecules

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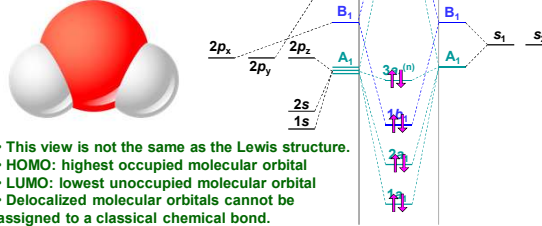
- The minimum base necessary to create the molecular orbitals of water:

Symmetry class	O atom orbitals	2H group orbitals
$A_1$	$1s, 2s, 2p_z$	$\chi_1$
$B_1$	$2p_x$	$\chi_2$
$B_2$	$2p_y$	-

- To create molecular orbitals, atomic orbital functions in the same symmetry class must be combined linearly.
- In each symmetry class, the number of independent molecular orbitals formed is the same as the number of orbitals ( $H_2O$ : 4  $A_1$ , 2  $B_1$ , 1  $B_2$ ). →MO correlation diagram (order of energy from calculation or measurement).


### Electron structure of molecules, MO correlation diagrams

Symmetry class	O atom orbitals	2H group orbitals
$A_1$	$1s, 2s, 2p_z$	$\chi_1$
$B_1$	$2p_x$	$\chi_2$
$B_2$	$2p_y$	-



- This view is not the same as the Lewis structure.
- HOMO: highest occupied molecular orbital
- LUMO: lowest unoccupied molecular orbital
- Delocalized molecular orbitals cannot be assigned to a classical chemical bond.

### Electron structure of molecules, the Hückel method



Erich Hückel (1896-1980)

- The simplest method capable of handling  $\pi$  electrons in quantum mechanics.
- The results are numerically imprecise, but the most phenomena in  $\pi$  electron systems are interpreted well (qualitatively).
- Postulate: every molecular orbital of  $\pi$  electrons is of  $H\psi = E\psi$  form.

Effective operator: the effect of nuclei,  $\sigma$  electrons, and the interaction of  $\pi$  electrons are taken into account simultaneously.

- The full energy of the  $\pi$  electrons:  $E = \sum_{k=1}^K v_k E_k$   
Number of electrons on orbital  $k$
- The molecular orbitals are constructed from the linear combination of atomic orbitals using the principle of variation.

### Electron structure of molecules, the Hückel method

- Example: **ethylene**
- The  $\pi$  orbitals are formed from the  $p_z$  orbitals of the two carbon atoms.
- The energy of the orbitals are the solutions of the following equations:

$$\begin{vmatrix} m & 1 \\ 1 & m \end{vmatrix} = m^2 - 1 = 0 \quad \text{where} \quad m = \frac{\alpha - E}{\beta}$$

- Possible energies:  $E_1 = \alpha + \beta$  and  $E_2 = \alpha - \beta$  where  $E_1 < E_2$
- Normalized  $\pi$  orbitals:

$$\varphi_1 = \frac{1}{\sqrt{2}}(\chi_1 + \chi_2) \quad \text{és} \quad \varphi_2 = \frac{1}{\sqrt{2}}(\chi_1 - \chi_2)$$

bonding orbital      antibonding orbital

The  $p_z$  orbitals of individual C atoms

- In the ground state, the bonding orbital is doubly occupied, so the full  $\pi$ -energy:  $E = 2\alpha + 2\beta$

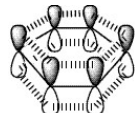
### Electron structure of molecules, the Hückel method

- The method presented for **ethylene** can be used for the  $\pi$  molecular orbitals of every aliphatic and cyclic conjugated.
- The  $\pi$  orbitals are constructed from the  $p_z$  orbitals of the carbon atoms.

$$\begin{vmatrix} m & 1 & 0 & 0 \\ 1 & m & 1 & 0 \\ 0 & 1 & m & 1 \\ 0 & 0 & 1 & m \end{vmatrix} = m^4 - 3m^2 + 1 = 0$$

butadiene

benzene  
The base consists of the  $p_z$  orbitals of the carbon atoms:




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butadiene benzene

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$$\begin{vmatrix} m & 1 & 0 & 0 & 0 & 1 \\ 1 & m & 1 & 0 & 0 & 0 \\ 0 & 1 & m & 1 & 0 & 0 \\ 0 & 0 & 1 & m & 1 & 0 \\ 0 & 0 & 0 & 1 & m & 1 \\ 1 & 0 & 0 & 0 & 1 & m \end{vmatrix} = m^6 - 6m^4 + 9m^2 - 4 = 0$$


### Electron structure of molecules, the valence bond (VB) method

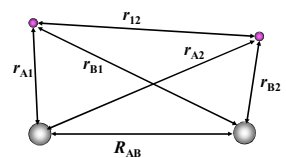
- In essence, the quantum mechanical version of the Lewis electron pair theory.
- Foundation: results of Heitler and London for the quantum mechanical description of  $H_2$  published in 1927.
- Development: Slater and Pauling (HLSP method)



Walter Heinrich Heitler (1904-1981)    Fritz Wolfgang London (1900-1954)    John Clarke Slater (1900-1976)    Linus Carl Pauling (1901-1994)

### Electron structure of molecules, the valence bond (VB) method

- The stationary Schrödinger equation of the  $H_2$  molecule:

$$-\frac{\hbar^2}{2\mu}(\Delta_1 + \Delta_2) + \frac{e^2}{4\pi\epsilon_0} \left( \frac{1}{r_{12}} + \frac{1}{R_{AB}} - \frac{1}{r_{A1}} - \frac{1}{r_{A2}} - \frac{1}{r_{B1}} - \frac{1}{r_{B2}} \right) \varphi = E\varphi$$


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- The total wave function of the electron forming the bond must be constructed considering four cases. The relevant wave functions:

1) $\begin{matrix} \textcircled{1} & \textcircled{2} \\ \text{H} & \text{H} \\ \text{A} & \text{B} \end{matrix}$ $f_1(1,2) = \varphi_A(1)\varphi_B(2)$	2) $\begin{matrix} \textcircled{2} & \textcircled{1} \\ \text{H} & \text{H} \\ \text{A} & \text{B} \end{matrix}$ $f_2(1,2) = \varphi_A(2)\varphi_B(1)$
3) $\begin{matrix} \textcircled{+} & \textcircled{-} \\ \text{H} & \text{H} \\ \text{A} & \text{B} \end{matrix}$ $f_3(1,2) = \varphi_A(1)\varphi_A(2)$	4) $\begin{matrix} \textcircled{+} & \textcircled{-} \\ \text{H} & \text{H} \\ \text{A} & \text{B} \end{matrix}$ $f_4(1,2) = \varphi_B(1)\varphi_B(2)$

Atomic orbitals of individual H atoms

### Electron structure of molecules, the valence bond (VB) method


- The total wave function of the electron pair is the linear combination of the wave functions corresponding to the individual cases:  
 $\varphi(1,2) = c_1f_1 + c_2f_2 + c_3f_3 + c_4f_4 = f_1 + f_2 + c(f_3 + f_4)$
- By the principle of variation,  $c$ ,  $\varphi(1,2)$  and  $E$  can be calculated.

1) $\begin{matrix} \textcircled{1} & \textcircled{2} \\ \text{H} & \text{H} \\ \text{A} & \text{B} \end{matrix}$ $f_1(1,2) = \varphi_A(1)\varphi_B(2)$	2) $\begin{matrix} \textcircled{2} & \textcircled{1} \\ \text{H} & \text{H} \\ \text{A} & \text{B} \end{matrix}$ $f_2(1,2) = \varphi_A(2)\varphi_B(1)$
3) $\begin{matrix} \textcircled{+} & \textcircled{-} \\ \text{H} & \text{H} \\ \text{A} & \text{B} \end{matrix}$ $f_3(1,2) = \varphi_A(1)\varphi_A(2)$	4) $\begin{matrix} \textcircled{+} & \textcircled{-} \\ \text{H} & \text{H} \\ \text{A} & \text{B} \end{matrix}$ $f_4(1,2) = \varphi_B(1)\varphi_B(2)$

1s atomic orbitals of the individual H atoms (ground state)

### Electron structure of molecules, the valence bond (VB) method

- A molecule with more complex bonding scheme: benzene
- When the full wave function of the molecule is created, several different options for pairing up electron to form bonds must be considered.



- In the VB method, the full wave function of the benzene molecule:  
 $\Psi = c_1(\Psi_1 + \Psi_2) + c_2(\Psi_3 + \Psi_4 + \Psi_5)$
- Coefficients  $c_1, c_2$  and ground state  $E$  can be calculated using the principle of variation

### Electron structure of molecules

<b>MO method</b> <ul style="list-style-type: none"> <li>• Computes orbitals.</li> <li>• Originally delocalized orbitals become localized.</li> <li>• Easier to implement computationally.</li> </ul>		<b>VB method</b> <ul style="list-style-type: none"> <li>• Orbitals, orbital energies are meaningless.</li> <li>• A combination of localized structures is used to delocalize electrons.</li> <li>• Single electron bonds and excited states are difficult to deal with.</li> <li>• For large molecules, enumerating and considering the resonance structures might be a challenge.</li> </ul> <p>→ The VB method had secondary importance for a long time, but today is on the rise again (equivalent to the MO method).</p>
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### Electron structure of molecules, hybridization

- Hybrid orbitals are useful mostly for the qualitative interpretations of molecular geometry.
- They are formed by the linear combination of orbitals on a single atom.
- The hybrid orbital group corresponding to the geometry of the entire molecule has a pre-determined symmetry.
- Geometry of **methane**: excellent interpretation by  $sp^3$  hybrid orbitals

Atomic orbitals of the carbon atom

$1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0$      $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$      $1s^2 h_1^1 h_2^1 h_3^1 h_4^1$

### Electron structure of molecules, hybridization

- There is no experimental evidence to support the  $2s^1 2p_x^1 2p_y^1 2p_z^0$  excited state.
- Hybrid orbitals are equivalent, their charge density is the same, only the orientation is different.

Atomic orbitals of the carbon atom

$1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0$      $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$      $1s^2 h_1^1 h_2^1 h_3^1 h_4^1$

### Electron structure of molecules, hybridization

Chemical bonds are formed

Atomic orbitals of the carbon atom

$1s^2 2s^2 2p_x^1 2p_y^1 2p_z^0$      $1s^2 2s^1 2p_x^1 2p_y^1 2p_z^1$      $1s^2 h_1^1 h_2^1 h_3^1 h_4^1$

### Electron structure of molecules, hybridization

- Constructing the hybrid orbitals depends on the identity of atomic orbitals necessary to give a the hybrid group orbitals with pre-determined symmetry
- Group theories aids the selection of the appropriate atomic orbitals.
- Reducible representation:

$T_d$	$E$	$8C_3$	$3C_2$	$6S_4$	$6\sigma_d$
$\Gamma$	4	1	0	0	2

• Reduction gives the  $\Gamma = A_1 + T_2$  form.

• Character table: symmetry class  $A_1$  contains the  $s$  orbital, class  $T_2$  contains the  $(p_x, p_y, p_z)$  or  $(d_{xy}, d_{xz}, d_{yz})$  orbitals.

→ the possible hybridizations are  $sp^3$  or  $sd^3$ . For methane, the former is preferred energetically.

### Electron structure of molecules, hybridization

Number of atomic orbitals	shape	hybrid	example
2	linear	$sp$	$C_2H_2$
3	trigonal planar	$sp^2$	$C_2H_4, BF_3$
4	tetrahedral	$sp^3, sd^3$	$CH_4, NH_3, MnO_4^-$
4	square planar	$dsp^2$	$PCl_4^{2-}, Ni(CN)_4^{2-}$
5	trigonal pyramidal	$dsp^3$	$PCl_5, Fe(CO)_5$
6	octahedral	$d^2sp^3$	$PF_6^{2-}, CoF_6^{2-}$

- Hybridization – in the form of the combinations of the orbitals for a given atom – is included in the MO methods that use atomic orbitals as bases.