

# Molecules

**Molecular orbitals,  
geometry,  
and vibrations**

**March 17, 2022**

$$E = \frac{\langle \Psi | \hat{H} | \Psi \rangle}{\langle \Psi | \Psi \rangle}$$

## Born Oppenheimer Approximation:

$$\hat{H} = \hat{H}_{\text{elec}} + \hat{H}_{\text{nucl}}$$

**many electron wave  
function for given  
positions  $\mathbf{R}$  of nuclei**

**motion of nuclei**

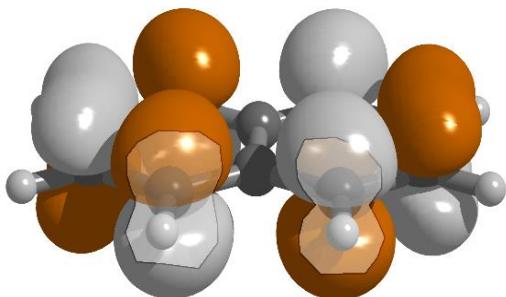
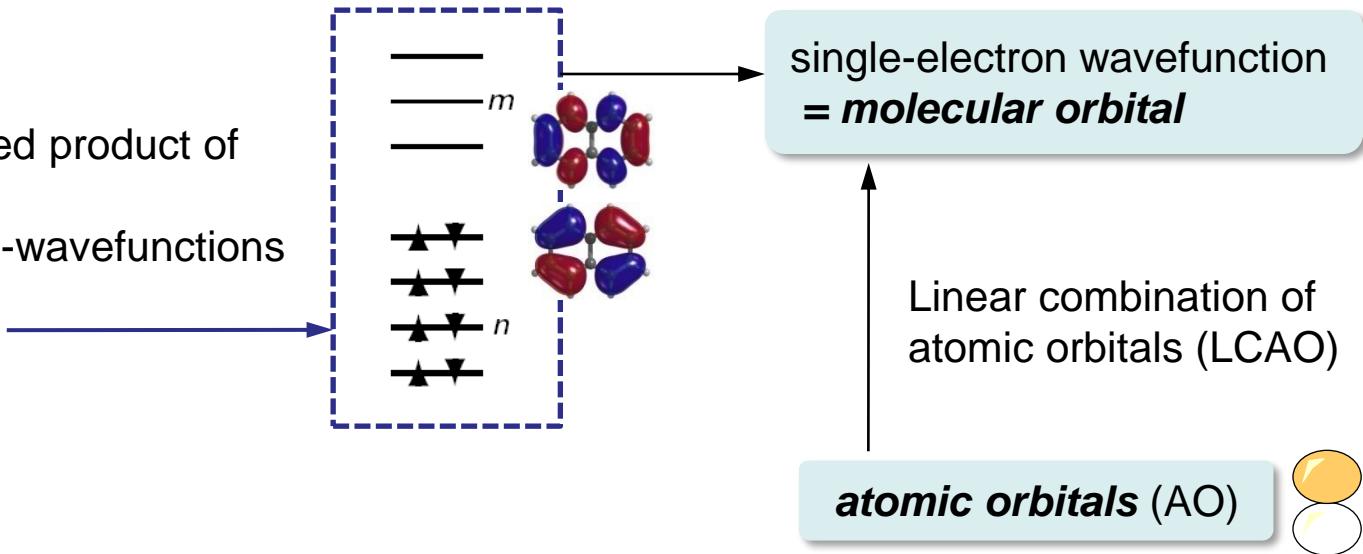
# Born Oppenheimer approximation

recap

many-electron wave function

for a given set of positions  $\mathbf{R}_A$

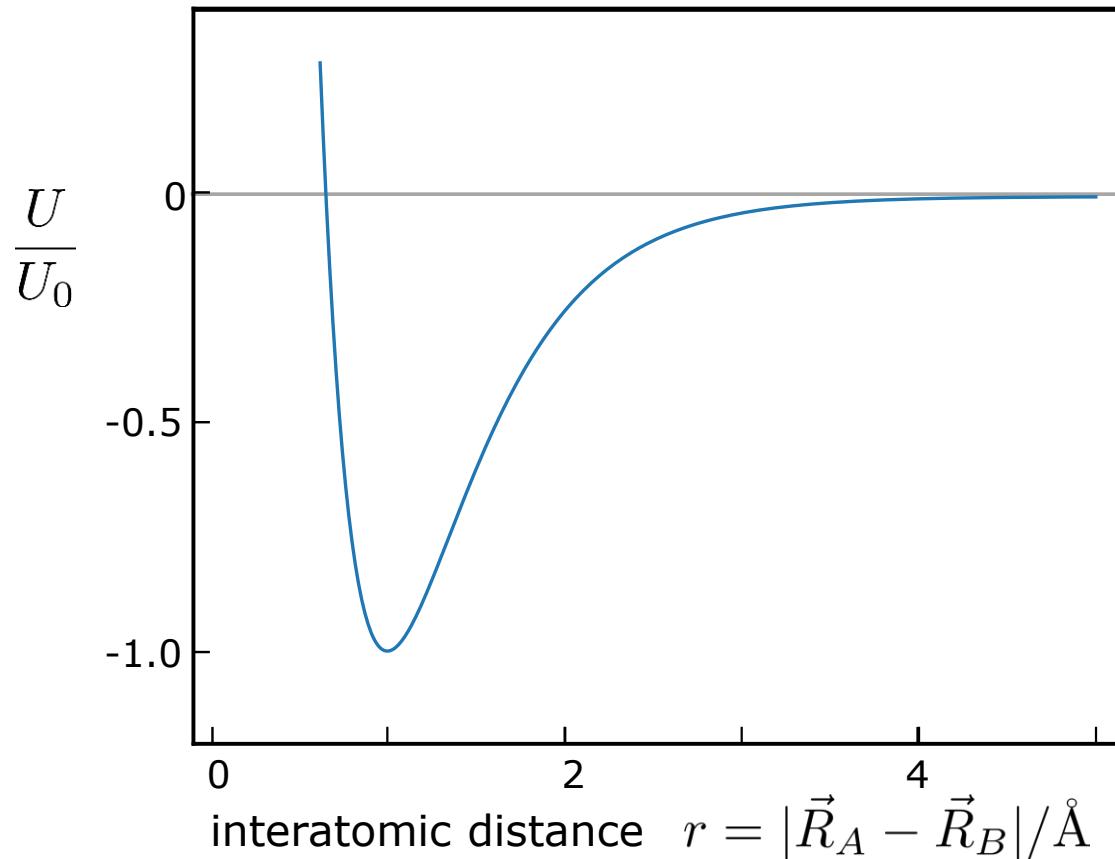
antisymmetrized product of  
**occupied**  
single electron-wavefunctions

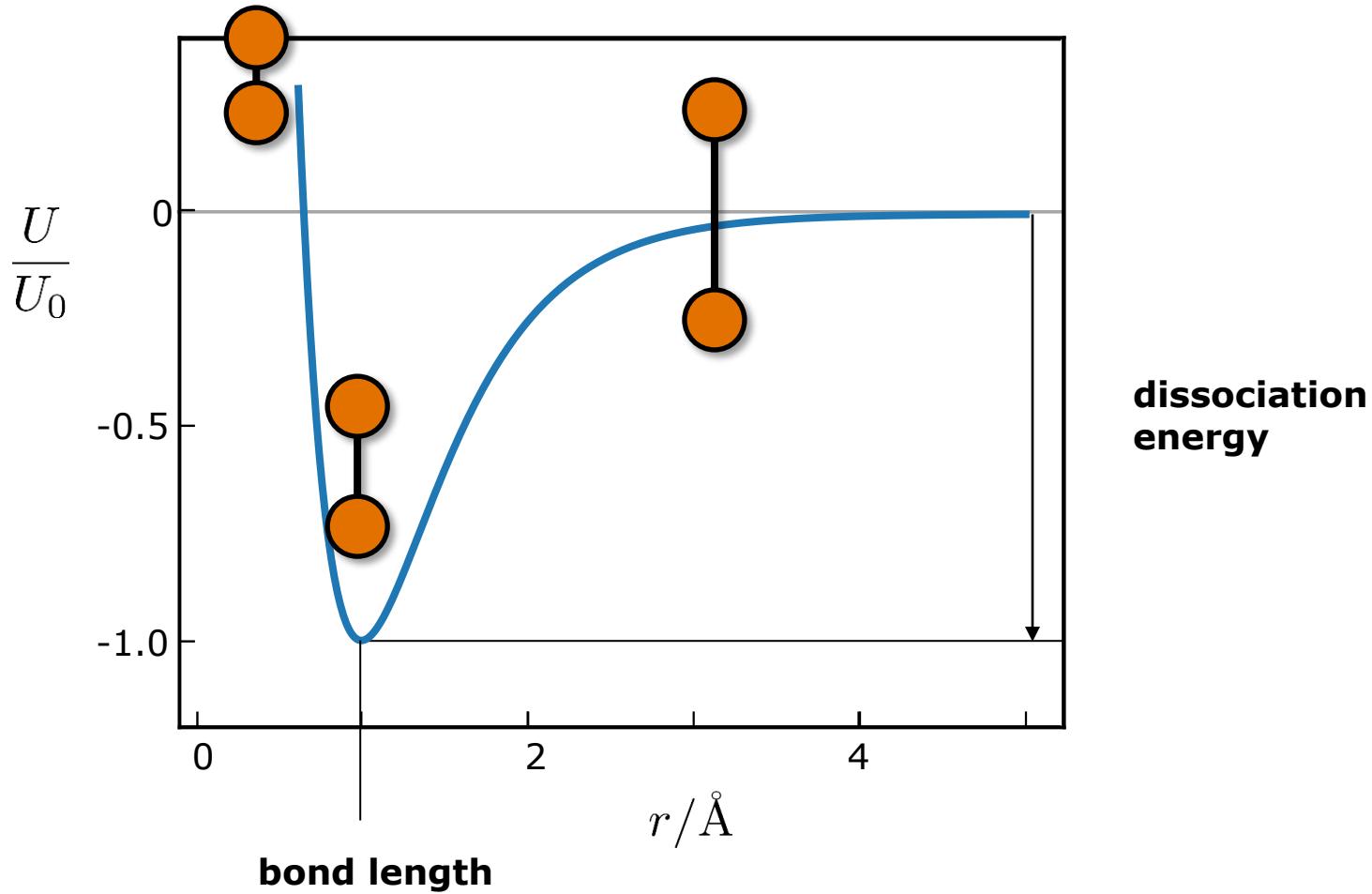


how AO contribute to each MO

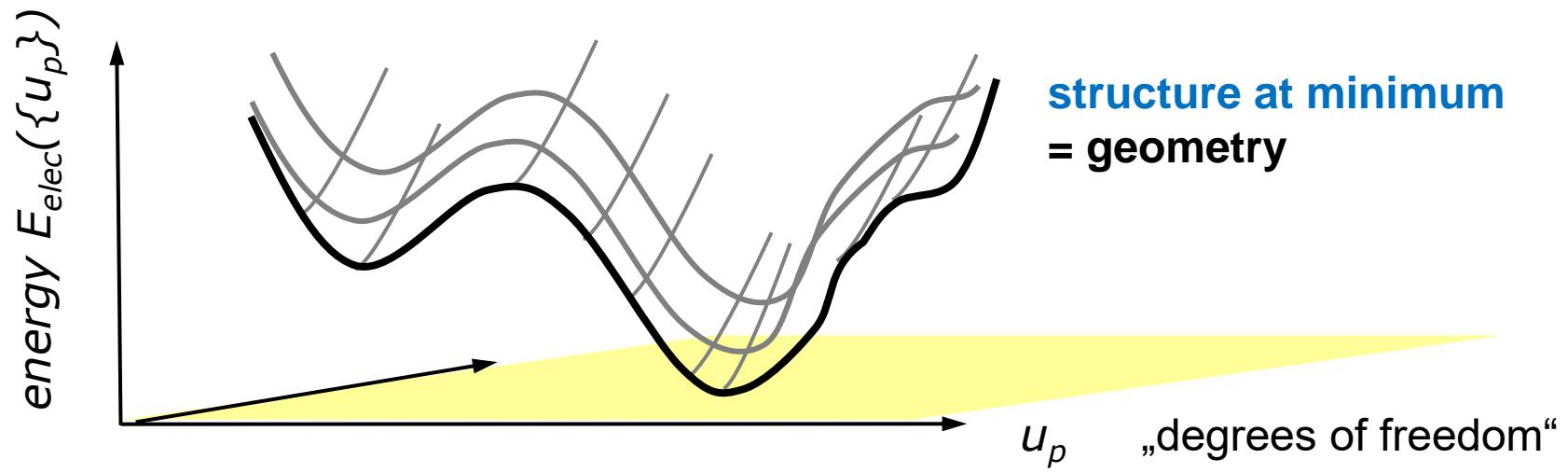
**electronic energy: serves as potential for nuclei**

$$\hat{H}\Psi(\vec{R}_A, \vec{R}_B) = \frac{\hbar^2}{2M} (\nabla_A^2 + \nabla_B^2) \Psi(\vec{R}_A, \vec{R}_B) + E_{\text{elec}}(r_{AB})\Psi(\vec{R}_A, \vec{R}_B)$$



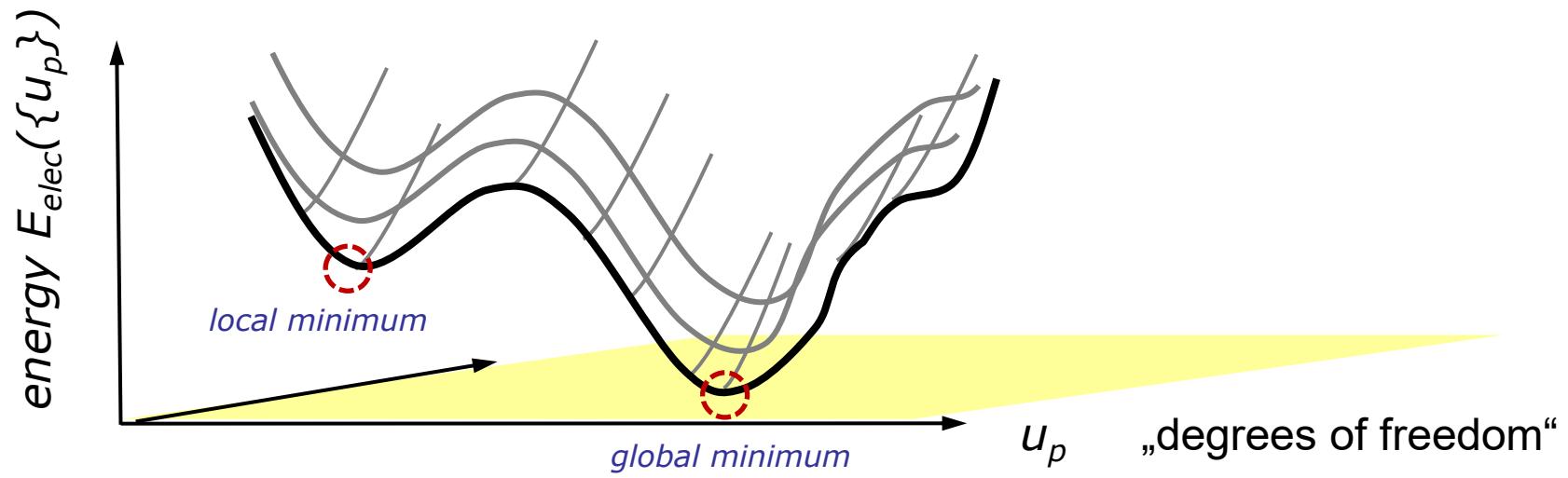
**bond potential in diatomic molecule**

nuclei move in potential energy surface



with respect to each degree of freedom

$$\frac{\partial E_{\text{elec}}}{\partial u_i} = 0$$



number of values to fully describe arrangement of atoms in space

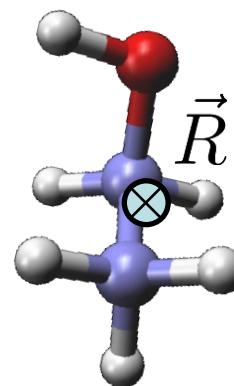
**n atoms :**

**3n degrees of freedom**

$$\hat{H} = \frac{\hbar^2}{2m} \nabla_R^2 + \sum_p \frac{\hbar^2}{2\mu_p} \nabla_{r_p}^2 + E_{\text{elec}}(r_1, \dots, r_{3n-3})$$

center of mass

$\vec{R}$



relative coordinates:  $r_p$   
reduced mass  $\mu$

3 rotations  
3n-6 internal  
degrees of freedom

number of values to fully describe arrangement of atoms in space

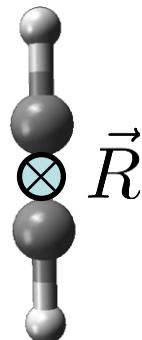
**n atoms :**

**3n degrees of freedom**

$$\hat{H} = \frac{\hbar^2}{2m} \nabla_R^2 + \sum_p \frac{\hbar^2}{2\mu_p} \nabla_{r_p}^2 + E_{\text{elec}}(r_1, \dots, r_{3n-3})$$

center of mass

$\vec{R}$



3 translations

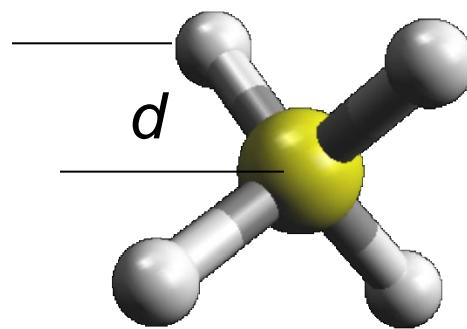
relative coordinates:  $r_p$   
reduced mass  $\mu$



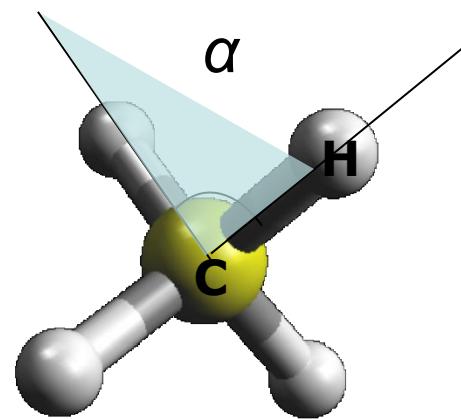
2 rotations  
3n-5 internal  
degrees of freedom

**3n-6 internal degrees of freedom**

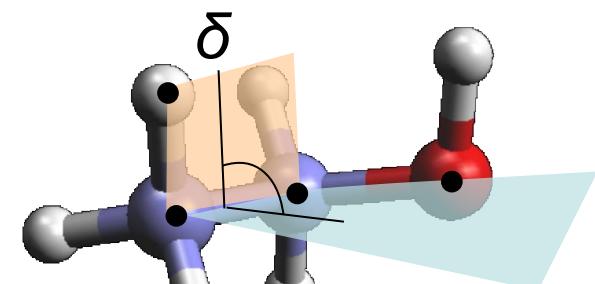
bond length



bond angles



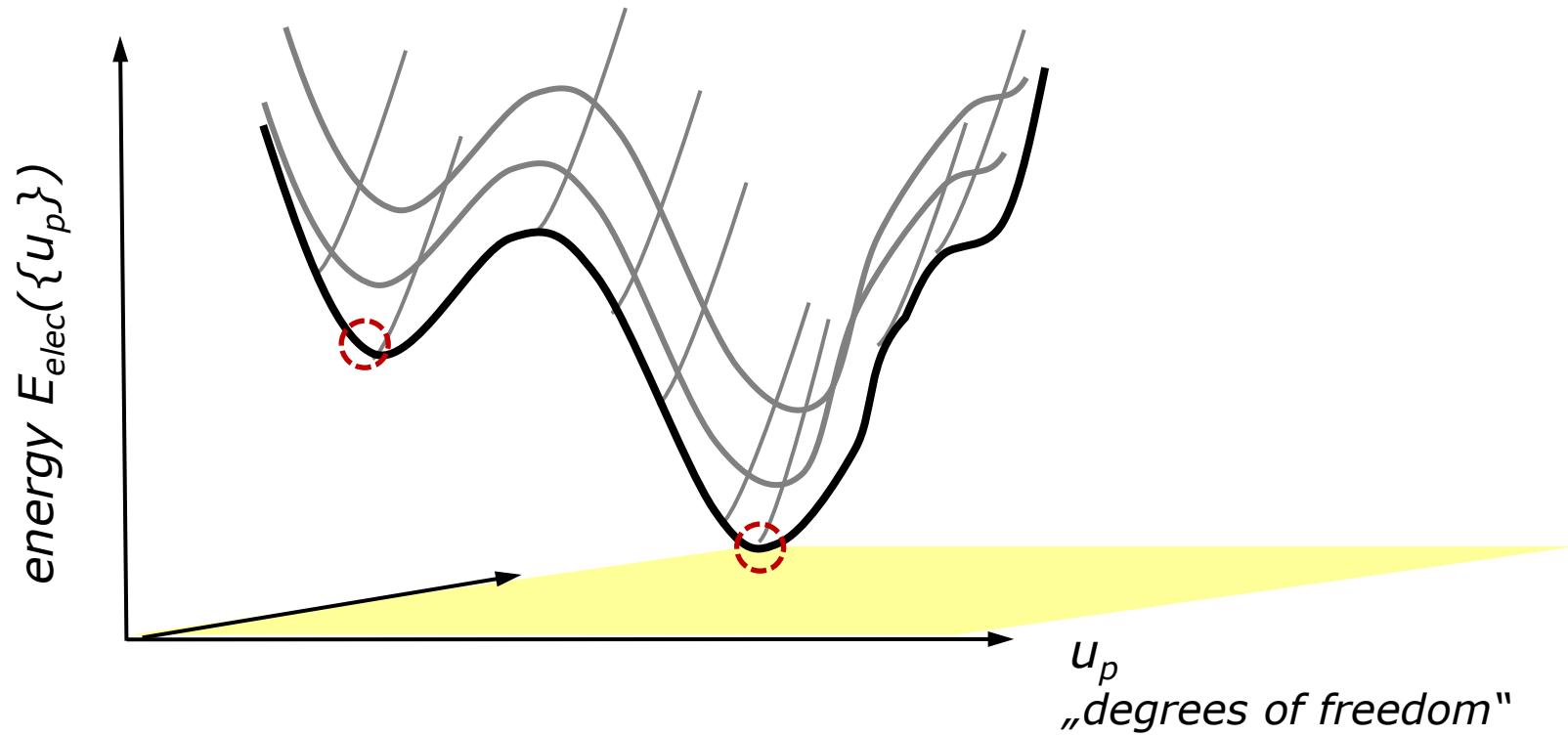
dihedral angles

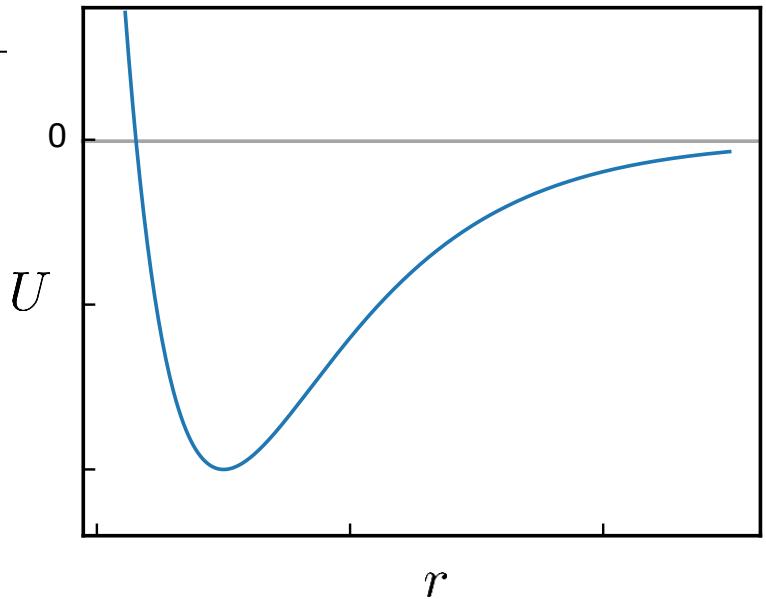


(stretching/compression)

(torsions)

move with reduced mass of involved atoms

**motion near minima?**



**Morse  
(covalent)**

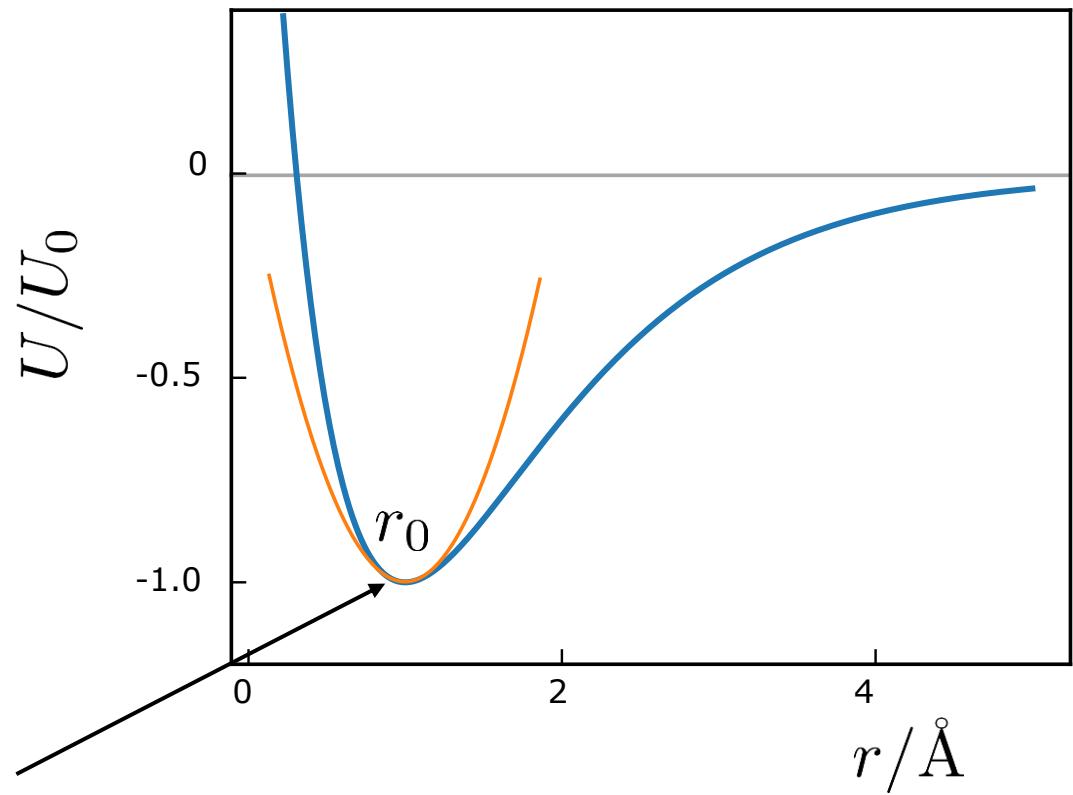
$$U(r) = U_0 \left( e^{-2a(r-r_0)} - 2e^{-a(r-r_0)} \right)$$

**Lennard-Jones  
(van der Waals)**

$$U(r) = 4\epsilon \left( \left(\frac{\sigma}{r}\right)^{12} - \left(\frac{\sigma}{r}\right)^6 \right)$$

**Morse potential**

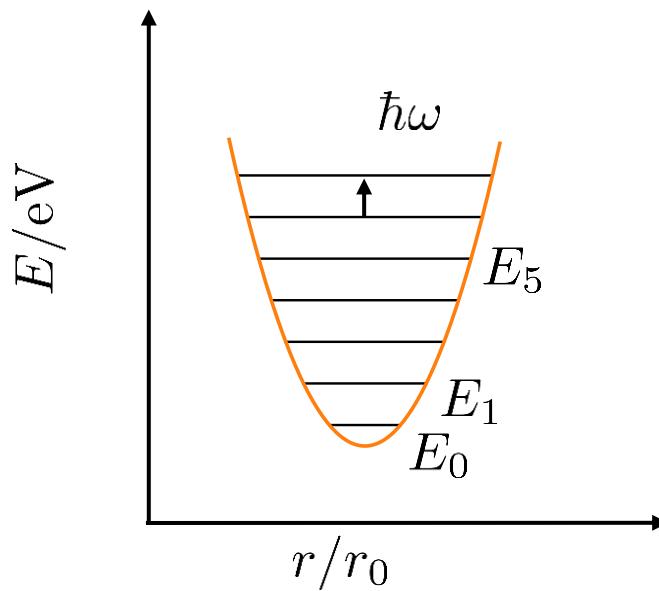
$$U(r) = U_0 \left( e^{-2a(r-r_0)} - 2e^{-a(r-r_0)} \right)$$



$$U(r) - U_0 \approx U_0 a^2 (r - r_0)^2 + \dots$$

**harmonic oscillator**

$$U_{\text{h-o}}(r) = \frac{k_{\text{eff}}}{2}(r - r_0)^2$$



$$E_n = \hbar\omega\left(n + \frac{1}{2}\right)$$

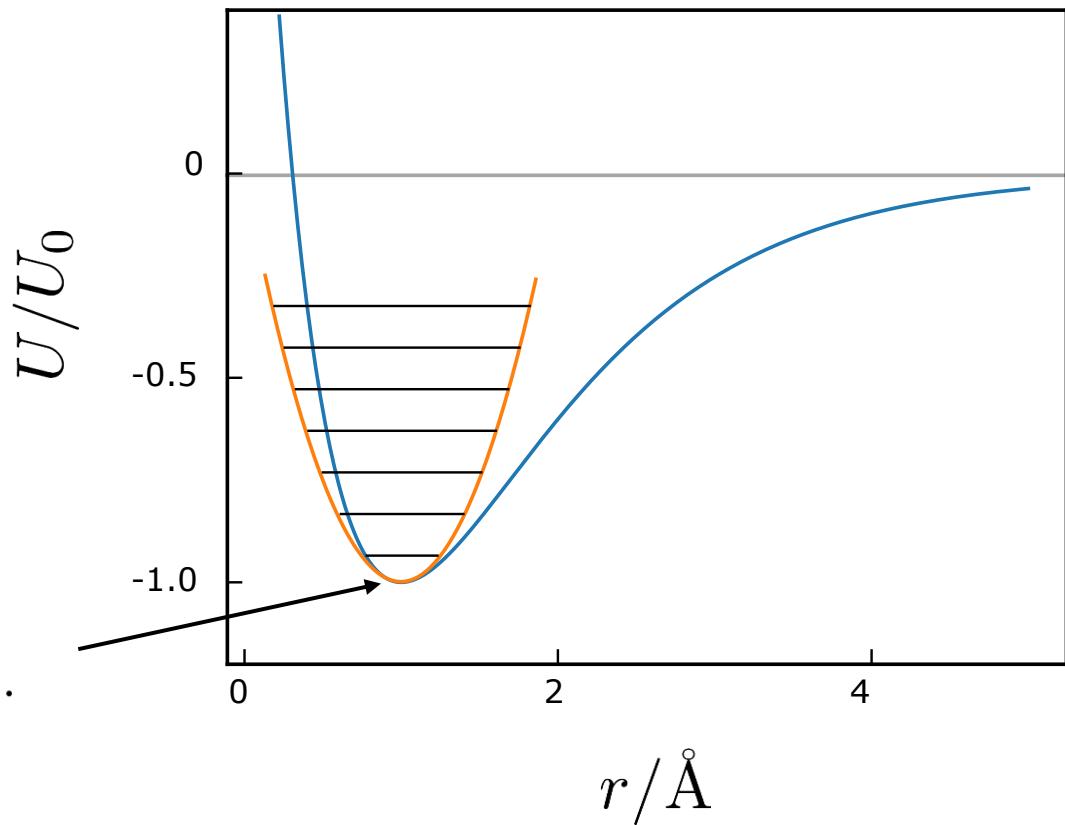
$$\omega = \sqrt{\frac{k_{\text{eff}}}{\mu}}$$

**Morse potential**

$$U(r) = U_0 \left( e^{-2a(r-r_0)} - 2e^{-a(r-r_0)} \right)$$

$$\omega = \sqrt{\frac{2U_0 a^2}{\mu}}$$

$$U(r) \approx U_0 a^2 (r - r_0)^2 + \dots$$



$$U(r) = U_0 \left( e^{-2a(r-r_0)} - 2e^{-a(r-r_0)} \right) \quad \text{as potential in} \quad \hat{H}_{\text{Morse}}$$

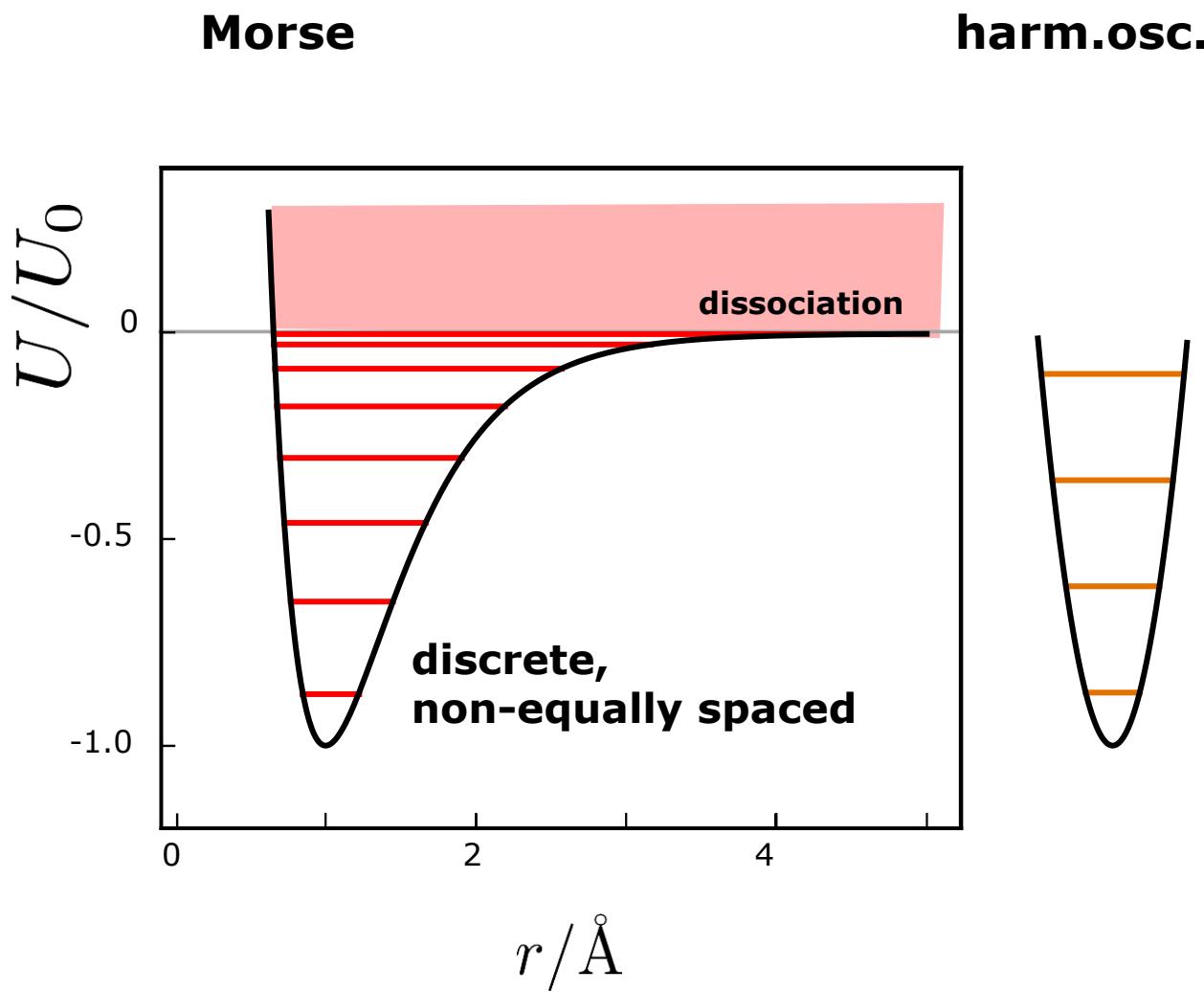
ansatz for wavefunction: linear combination of harmonic oscillator states

$$|\psi_{\text{LCHM}}\rangle = c_0 |\phi_0\rangle + c_1 |\phi_1\rangle + c_2 |\phi_2\rangle + \dots$$

eigenvalue problem

eigenenergies = energy of vibrational levels

$$E_n = \hbar\omega \left( n + \frac{1}{2} - \frac{1}{2} \sqrt{\frac{a}{2\mu U_0}} \left( n + \frac{1}{2} \right)^2 \right)$$



excite vibrations via ?

$$U(r) = U_0 \left( e^{-2a(r-r_0)} - 2e^{-a(r-r_0)} \right)$$

ansatz for wavefunction: linear combination of harmonic oscillator states

$$|\psi_{\text{LCHM}}\rangle = c_0 |\phi_0\rangle + c_1 |\phi_1\rangle + c_2 |\phi_2\rangle + \dots$$

$$\hat{H}_{\text{morse}} |\psi_{\text{LCHM}}\rangle = E |\psi_{\text{LCHM}}\rangle$$

$$\langle \phi_0 | \hat{H}_{\text{morse}} | \psi_{\text{LCHM}} \rangle = E \langle \phi_0 | \psi_{\text{LCHM}} \rangle$$

$$c_0 \langle \phi_0 | \hat{H}_{\text{morse}} | \phi_0 \rangle + c_1 \langle \phi_0 | \hat{H}_{\text{morse}} | \phi_1 \rangle \dots = E c_0 \langle \phi_0 | \phi_0 \rangle + E c_1 \langle \phi_0 | \phi_1 \rangle \dots +$$

$$c_0 \langle \phi_j | H_{\text{morse}} | \phi_0 \rangle + c_1 \langle \phi_j | H_{\text{morse}} | \phi_1 \rangle \dots = E c_j$$

$$|\psi_{\text{LCHM}}\rangle = c_0|\phi_0\rangle + c_1|\phi_1\rangle + c_2|\phi_2\rangle + \dots$$

$$\hat{H}_{\text{morse}}|\psi_{\text{LCHM}}\rangle = E|\psi_{\text{LCHM}}\rangle$$

$$\langle\phi_0|\hat{H}_{\text{morse}}|\psi_{\text{LCHM}}\rangle = E\langle\phi_0|\psi_{\text{LCHM}}\rangle$$

$$c_0\langle\phi_0|\hat{H}_{\text{morse}}|\phi_0\rangle + c_1\langle\phi_0|\hat{H}_{\text{morse}}|\phi_1\rangle \dots = Ec_0\langle\phi_0|\phi_0\rangle + Ec_1\langle\phi_0|\phi_1\rangle \dots$$

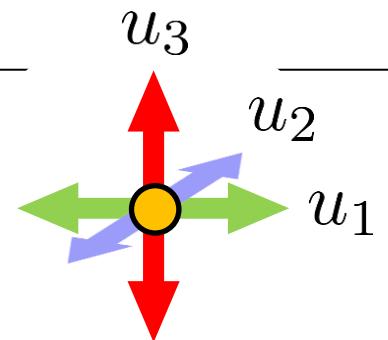
$$c_0\langle\phi_j|\hat{H}_{\text{morse}}|\phi_0\rangle + c_1\langle\phi_j|\hat{H}_{\text{morse}}|\phi_1\rangle \dots = Ec_j$$

$$H_{ij} = \langle\phi_i|\hat{H}_{\text{morse}}|\phi_j\rangle$$

$$\begin{pmatrix} H_{00} & H_{01} & \dots \\ H_{10} & H_{11} & \dots \\ H_{20} & H_{21} & \dots \\ \vdots & \vdots & \end{pmatrix} \begin{pmatrix} c_0 \\ c_1 \\ c_2 \\ \dots \end{pmatrix} = E \begin{pmatrix} c_0 \\ c_1 \\ c_2 \\ \dots \end{pmatrix}$$

Eigenvalues =  
energies of vibrational  
levels

in cartesian coordinates



$$m_1 \frac{d^2 u_1}{dt^2} = k_{12}(u_2 - u_1) + k_{13}(u_3 - u_1) + \dots + k_{1,3n}(u_{3n} - u_1)$$

$$m_1 \frac{d^2 u_2}{dt^2} = k_{12}(u_1 - u_2) + k_{23}(u_3 - u_2) + \dots + k_{2,3n}(u_{3n} - u_2)$$

$$m_1 \frac{d^2 u_3}{dt^2} = k_{13}(u_1 - u_3) + k_{23}(u_2 - u_3) + \dots + k_{3,3n}(u_{3n} - u_3)$$

$$m_2 \frac{d^2 u_4}{dt^2} = k_{14}(u_1 - u_4) + k_{24}(u_2 - u_4) + \dots + k_{4,3n}(u_{3n} - u_4)$$

⋮

$$m_n \frac{d^2 u_{3n-2}}{dt^2} = k_{1,3n-2}(u_1 - u_{3n-2}) + k_{2,3n-2}(u_2 - u_{3n-2}) + \dots + k_{3n-2,3n}(u_{3n} - u_{3n-2})$$

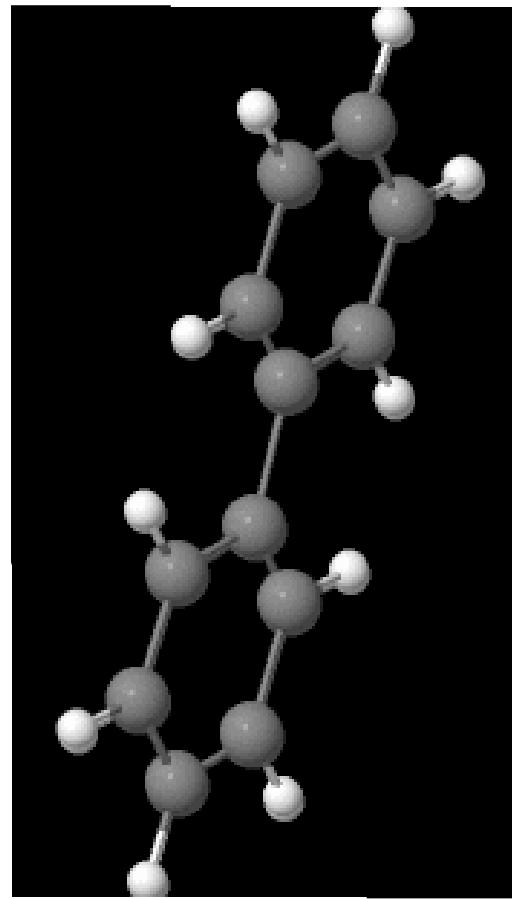
$$m_n \frac{d^2 u_{3n-1}}{dt^2} = k_{1,3n-1}(u_1 - u_{3n-1}) + k_{2,3n-1}(u_2 - u_{3n-1}) + \dots + k_{3n-1,3n}(u_{3n} - u_{3n-1})$$

$$m_n \frac{d^2 u_{3n}}{dt^2} = k_{1,3n}(u_1 - u_{3n}) + k_{2,3n}(u_2 - u_{3n}) + \dots + k_{3n,3n-1}(u_{3n-1} - u_{3n})$$

**all elongations evolve with same frequency**

$$u_p = A_p e^{i\omega t}$$

$$p = 1, \dots, 3n$$



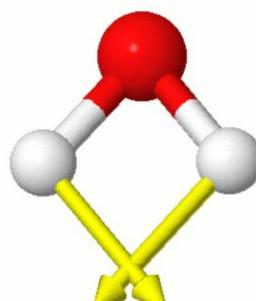
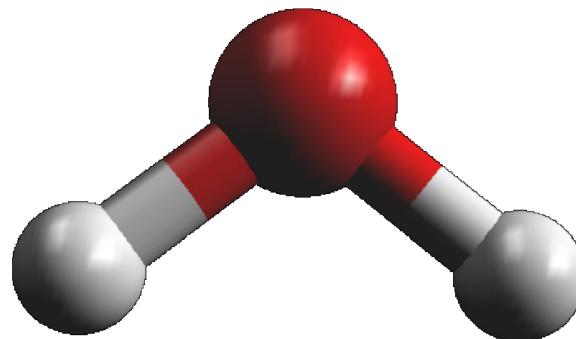
**all elongations evolve with same frequency**  $u_p = A_p e^{i\omega t}$

$$p = 1, \dots, 3n$$

$$\begin{bmatrix} \sum_{p \neq 1} \frac{k_{1p}}{m_1} & -\frac{k_{12}}{m_1} & -\frac{k_{13}}{m_1} & \cdots & -\frac{k_{1,3n}}{m_1} \\ -\frac{k_{21}}{m_1} & \sum_{p \neq 3} \frac{k_{2p}}{m_1} & -\frac{k_{2,3}}{m_1} & \cdots & -\frac{k_{2,3n}}{m_1} \\ -\frac{k_{31}}{m_1} & -\frac{k_{32}}{m_1} & \sum_{p \neq 3} \frac{k_{2p}}{m_1} & \cdots & -\frac{k_{3,3n}}{m_1} \\ \vdots & & & & \vdots \\ -\frac{k_{3n-2,1}}{m_n} & \cdots & \sum_{p \neq 3n-2} \frac{k_{3n-2,p}}{m_n} & -\frac{k_{3n-2,3n-1}}{m_n} & -\frac{k_{3n-2,3n}}{m_n} \\ -\frac{k_{3n-1,1}}{m_n} & \cdots & -\frac{k_{3n-1,3n-2}}{m_n} & \sum_{p \neq 3n-1} \frac{k_{3n-1,p}}{m_n} & -\frac{k_{3n-1,3n}}{m_n} \\ -\frac{k_{3n,1}}{m_n} & \cdots & -\frac{k_{3n,3n-2}}{m_n} & -\frac{k_{3n,3n-1}}{m_n} & \sum_{p \neq 3n} \frac{k_{3n,p}}{m_n} \end{bmatrix} \begin{bmatrix} A_1 \\ A_2 \\ A_3 \\ \vdots \\ A_{3n-2} \\ A_{3n-1} \\ A_{3n} \end{bmatrix} = \omega^2 \begin{bmatrix} A_1 \\ A_2 \\ A_3 \\ \vdots \\ A_{3n-2} \\ A_{3n-1} \\ A_{3n} \end{bmatrix}$$

**eigenvectors = “normal modes”, fundamental vibrations**

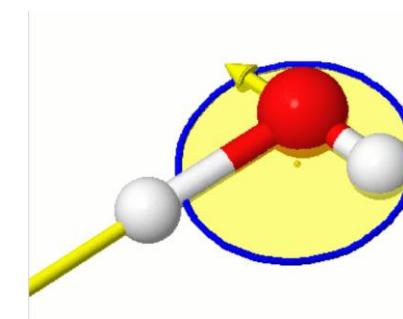
**eigenvalues = frequencies of normal modes**



H-O-H  
bending

$$\text{A1} \\ v_1 =$$

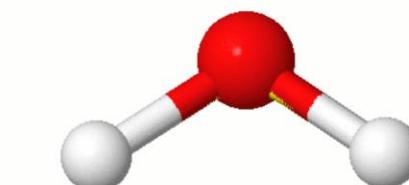
$$1711.15 \text{ cm}^{-1}$$



O-H  
asymmetric stretching

$$\text{B1} \\ v_3 =$$

$$3851.06 \text{ cm}^{-1}$$



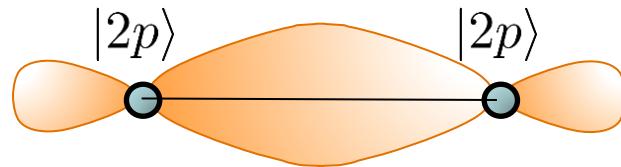
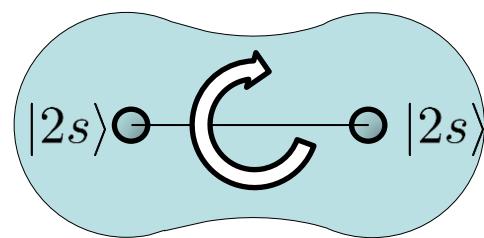
O-H  
symmetric stretching

$$\text{A1} \\ v_2 =$$

$$3730.03 \text{ cm}^{-1}$$

## **$\sigma$ bonds**

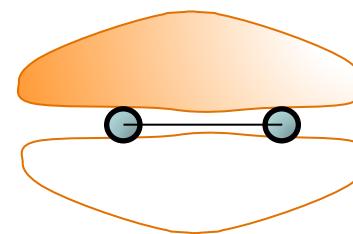
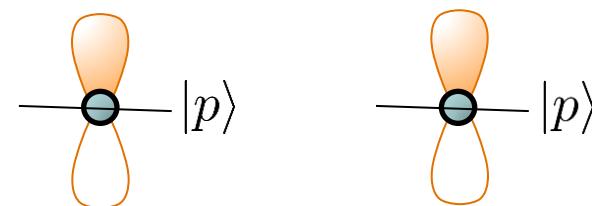
along interatomic axis (rotational symmetry)



angular momentum around interatomic axis = zero

## **$\pi$ bonds**

forms between two p orbitals

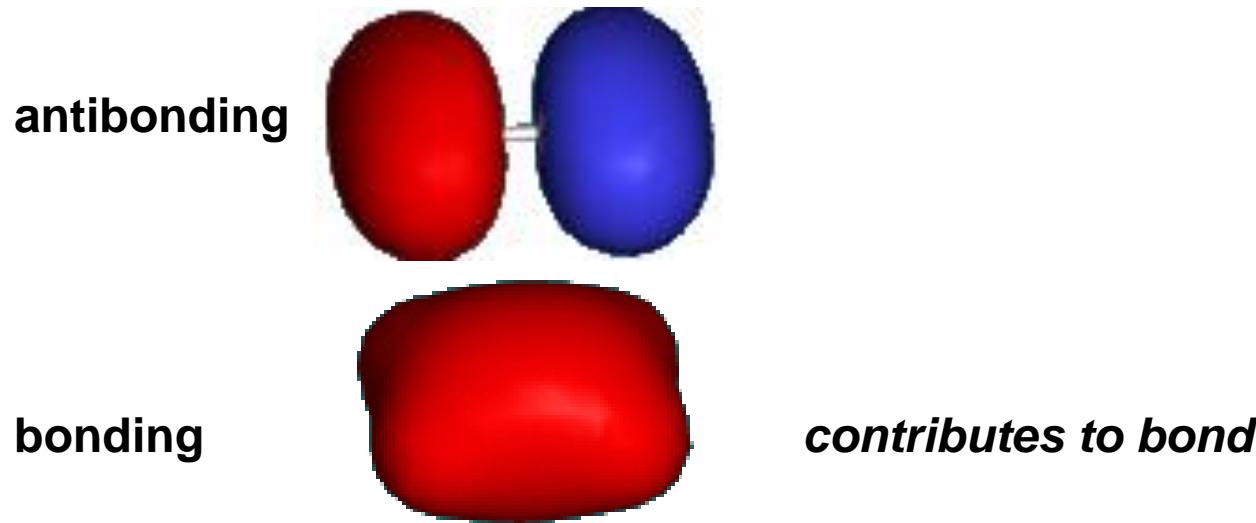


**parts of molecule can easily twist with respect to axis**

**molecule cannot twist around axis**

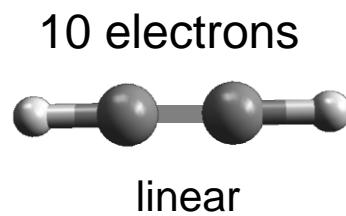
electron density between atoms: bond length and strength

occupied MO?



product of bonding and antibonding MO?

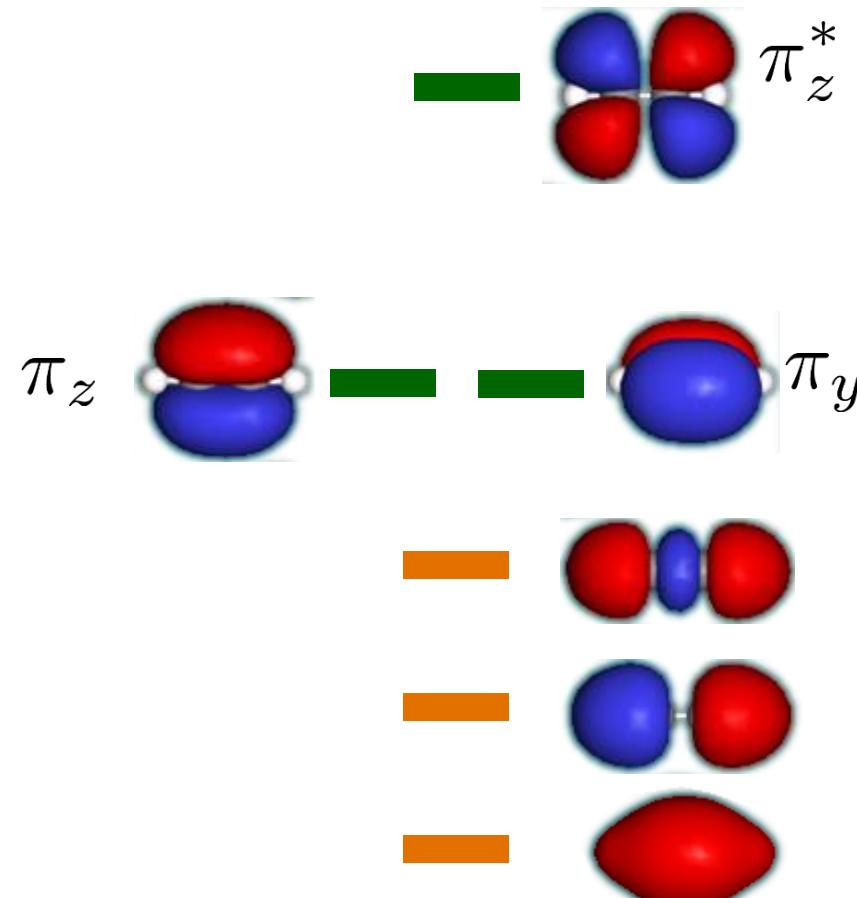
node in antibonding MO counteracts spread of electron density  
between atoms

**ethyne (acetylene)**

C C

triple bond

1.13 Å



**ethylene**

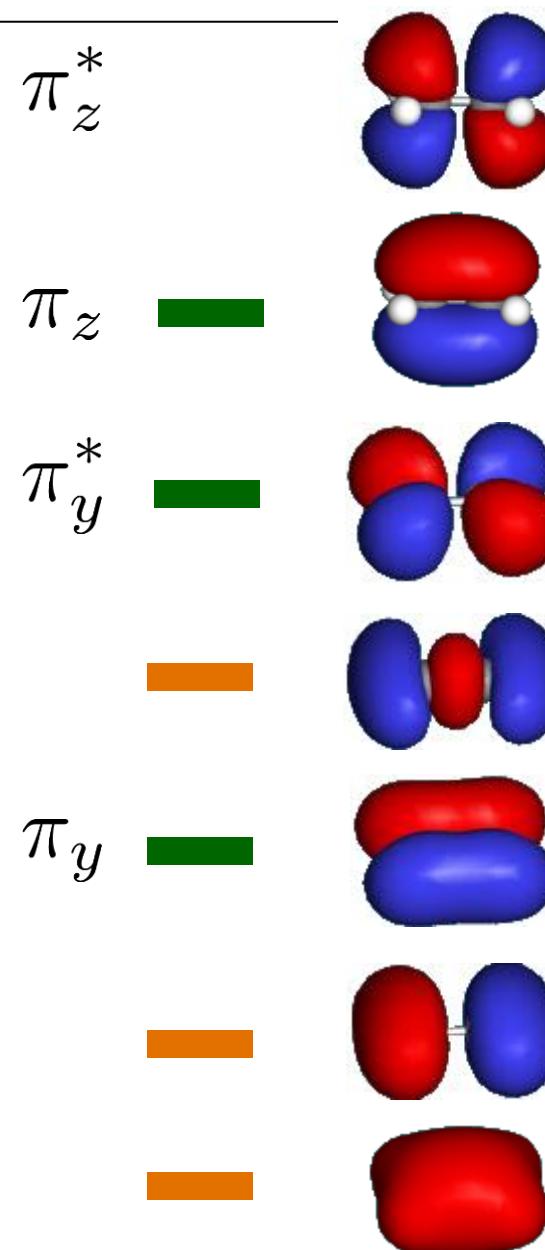
12 electrons

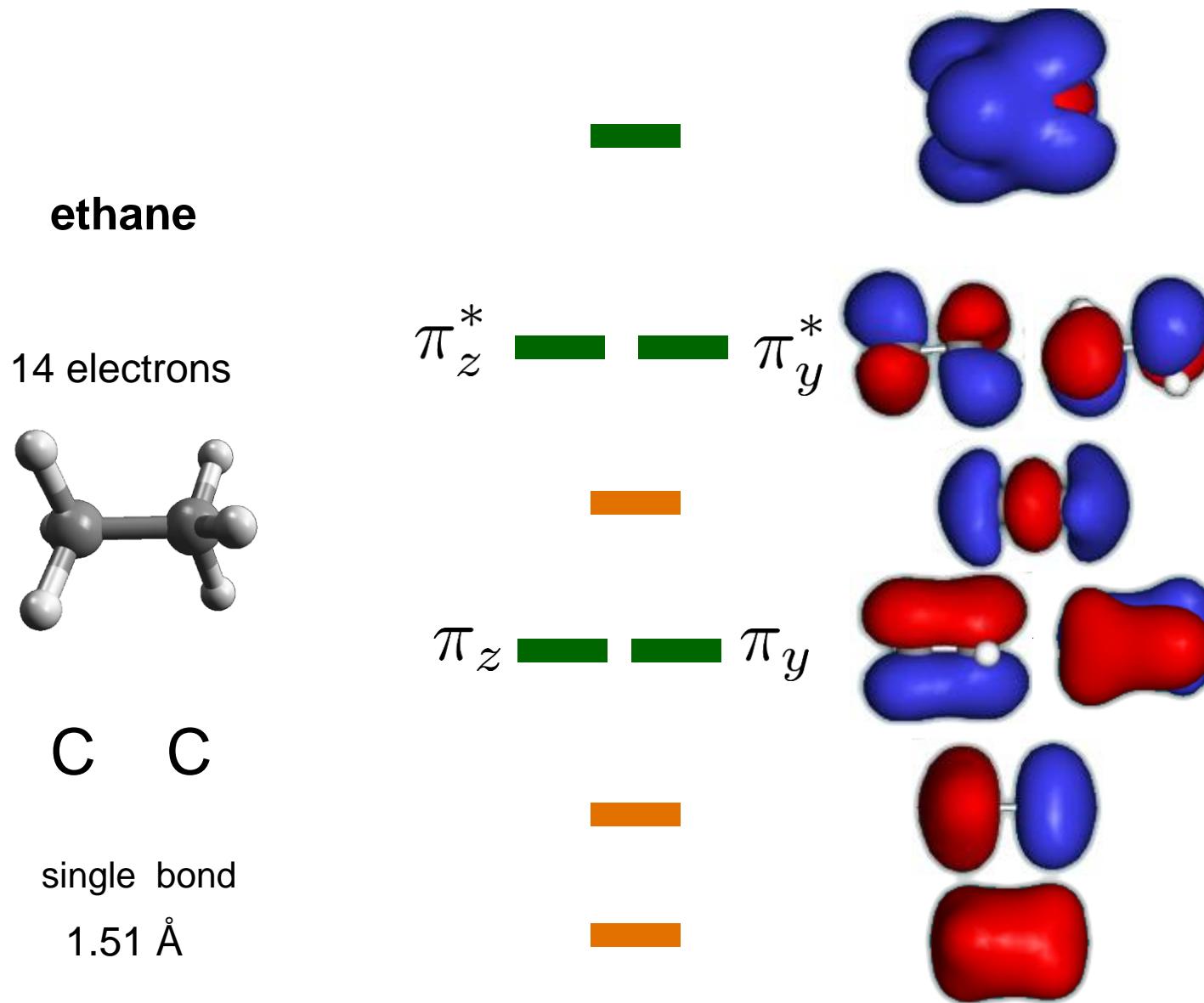


C C

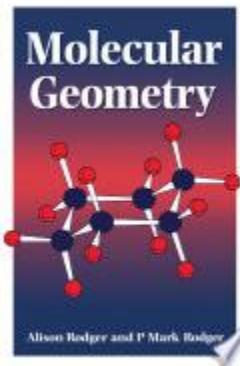
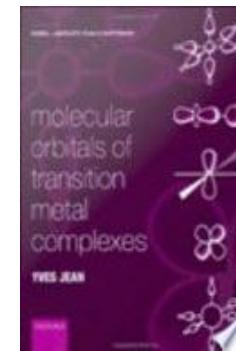
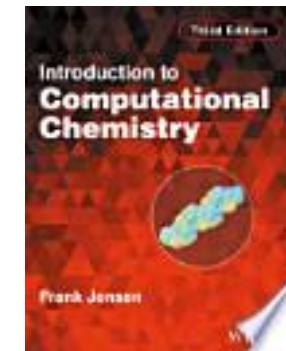
double bond

1.34 Å







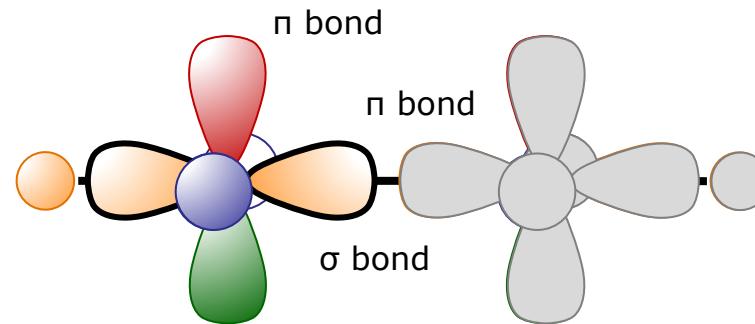
**Introduction****Molecular Geometry****Alison Rodger,  
Mark Rodger****Butterworth-  
Heinemann****Interpretation****Molecular Orbitals of Transition Metal Complexes****Yves Jean****Oxford  
University  
Press****D-I-Y****Introduction to Computational Chemistry****F. Jensen****WILEY & Sons**

## AO not participating in $\pi$ bonds

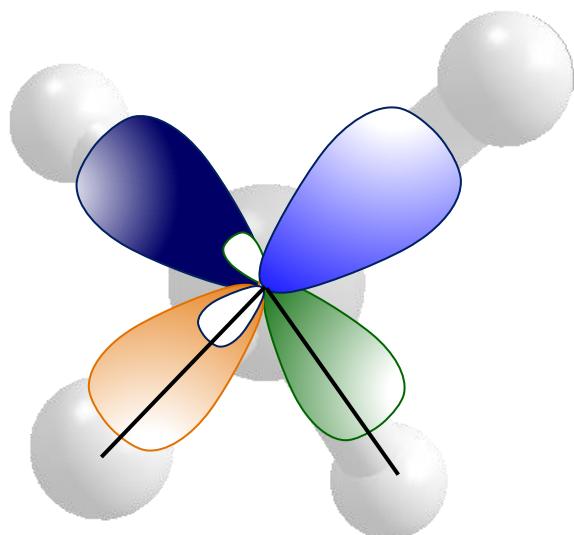
form

set of hybrid orbitals:

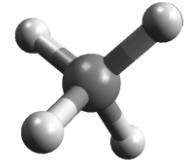
- identical in shape and energy
- each participates in one  $\sigma$  bond
- contain AO in fixed ratio



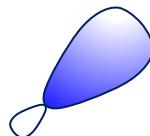
number of hybrid orbitals determines bond angles



109 deg

**methane**

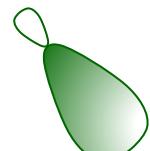
$$|\phi_1^{sp^3}\rangle = \frac{1}{2} (|2s\rangle + |2p_x\rangle + |2p_y\rangle + |2p_z\rangle)$$



$$|\phi_2^{sp^2}\rangle = \frac{1}{2} (|2s\rangle + |2p_x\rangle - |2p_y\rangle - |2p_z\rangle)$$

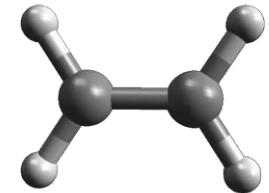


$$|\phi_3^{sp^3}\rangle = \frac{1}{2} (|2s\rangle - |2p_x\rangle - |2p_y\rangle + |2p_z\rangle)$$



$$|\phi_4^{sp^3}\rangle = \frac{1}{2} (|2s\rangle - |2p_x\rangle + |2p_y\rangle - |2p_z\rangle)$$

**four  $sp^3$  orbitals, tetrahedral**



ethylene

**each C atom: three in-plane  $sp^2$  orbitals**

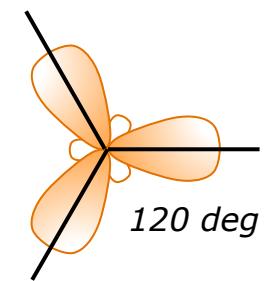
$$|\phi_1^{sp^2}\rangle = \frac{1}{\sqrt{3}} \left( |2s\rangle + \sqrt{2}|2p_x\rangle \right)$$

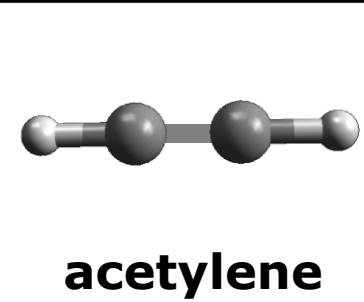
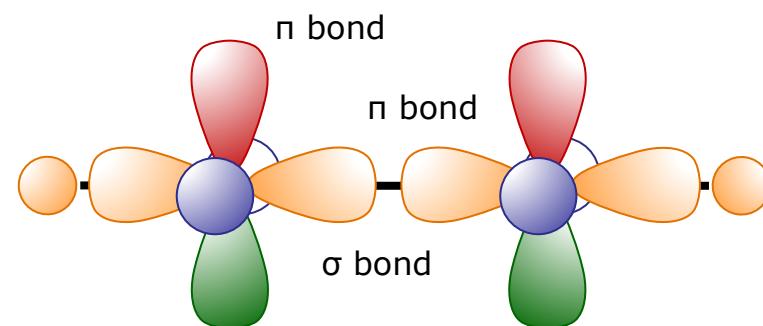


$$|\phi_2^{sp^2}\rangle = \frac{1}{\sqrt{3}}|2s\rangle - \frac{1}{\sqrt{6}}|2p_x\rangle + \frac{1}{\sqrt{2}}|2p_y\rangle$$

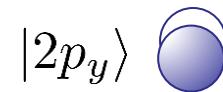
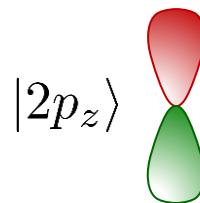
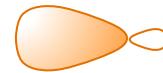


$$|\phi_3^{sp^2}\rangle = \frac{1}{\sqrt{3}}|2s\rangle - \frac{1}{\sqrt{6}}|2p_x\rangle - \frac{1}{\sqrt{2}}|2p_y\rangle$$

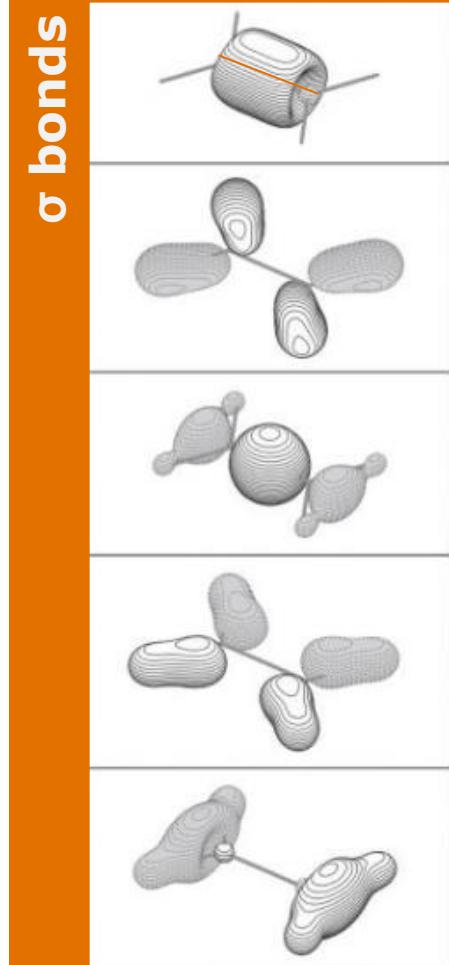
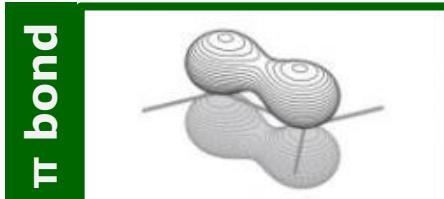
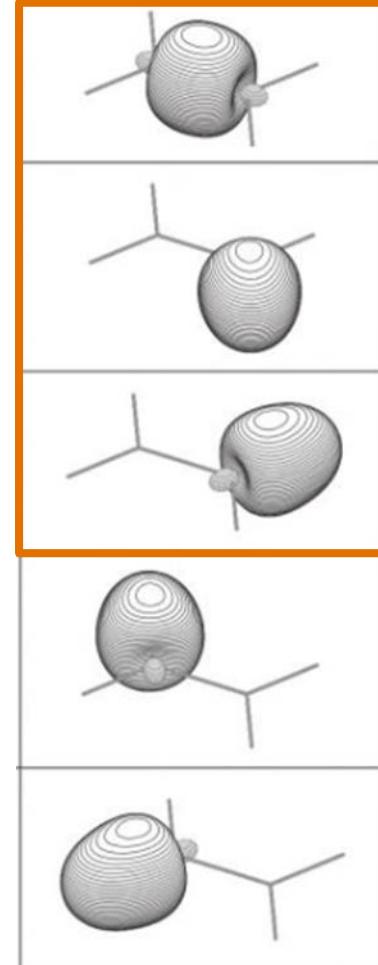
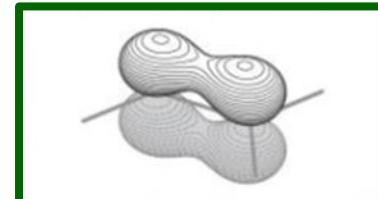




$$|\phi_1^{sp}\rangle = \frac{1}{\sqrt{2}} (|2s\rangle + |2p_x\rangle) \quad |\phi_2^{sp}\rangle = \frac{1}{\sqrt{2}} (|2s\rangle - |2p_x\rangle)$$



**two sp orbitals, linear = two σ-bonds along same axis**

**occupied MO****local contribution****AO C2**