

Units Units Units Units

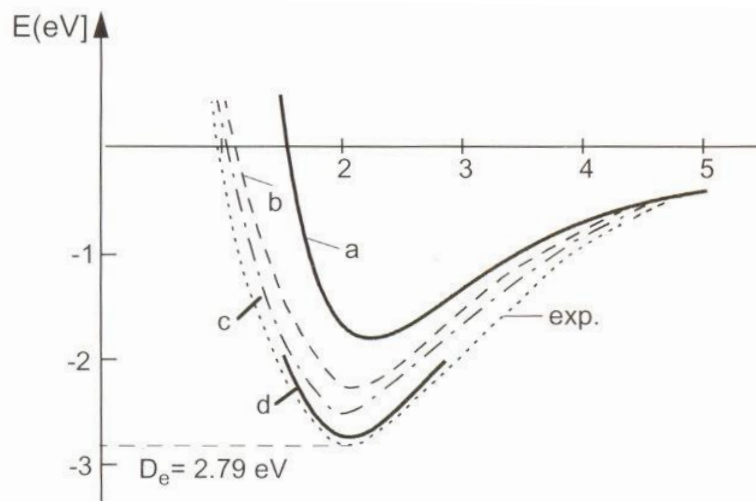


TABLE 10.2

Results of Various Calculations of the Ground-State Electronic Energy of H_2^+ ^a

ϕ	E_{\min}/E_h	R_{eq}/a_0
$1s(\zeta = 1.000)$	-0.564 83	2.49
$1s(\zeta = 1.238)$	-0.586 51	2.00
$1s(\zeta = 1.000) + a2p_z(\zeta = 1.000)$	-0.565 91	2.00
$1s(\zeta = 1.247) + b2p_z(\zeta = 1.247)$	-0.599 07	2.00
$1s(\zeta = 1.2458) + c2p_z(\zeta = 1.4224)$	-0.600 36	2.00
$1s(\zeta = 1.244) + c_12p_z(\zeta = 1.152) + c_23d_{z^2}(\zeta = 1.333)$ ^b	-0.6020	2.00
Exact ^c	-0.602 64	2.00

^a the table.
rk, 1977.
Molecular Ion.

TABLE 9.1

Atomic Units and Their SI Equivalents

Fig. 2.
with a)
term, z

Property	Atomic unit	SI equivalent
Mass	Mass of an electron, m_e	9.1094×10^{-31} kg
Charge	Charge on a proton, e	1.6022×10^{-19} C
Angular momentum	Planck constant divided by 2π , \hbar	1.0546×10^{-34} J·s
Length	Bohr radius, $a_0 = \frac{4\pi\epsilon_0\hbar^2}{m_e e^2}$	5.2918×10^{-11} m
Energy	$\frac{m_e e^4}{16\pi^2 \epsilon_0^2 \hbar^2} = \frac{e^2}{4\pi\epsilon_0 a_0} = E_h$	4.3597×10^{-18} J
Permittivity	$\kappa_0 = 4\pi\epsilon_0$	1.1127×10^{-10} C ² ·J ⁻¹ ·m ⁻¹

1 hartree

27.2114 eV

627.5095 kcal/mol

What is energy of
H⁺ and H?

Questions

- Why do we call adiabatic
- Delocalization and kinetic energy
- Why does using a smaller atomic wavefunction help?
- Why does adding a 2p orbital help but not 2S orbital?

Adiabatic Approximation

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Adiabatic process

From Wikipedia, the free encyclopedia

An **adiabatic process** is any process occurring without gain or loss of **heat** within a system (i.e. during the process the system is thermodynamically isolated- there is no heat transfer with the surroundings). This is the opposite of a **diabatic process**, where there *is* heat transfer. A key concept in **thermodynamics**, many rapid chemical and physical processes are described or approximated in this way. Such processes are usually followed or preceded by events that do involve **heat** transfer (i.e. are non-adiabatic). Examples include **electron-transfer**.

Adiabatic : no heat transfer between electron and nuclei

Heat: kinetic energy!

Kinetic energy of the nuclei does not effect the electron energies



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Questions

- Why do we call adiabatic
- Delocalization and kinetic energy
- Why does using a smaller atomic wavefunction help?
- Why does adding a 2p orbital help but not 2S orbital?

Answers Delocalization

- Now the electron distribution spreads, the position uncertainty increases. According to Uncertainty Principle, the momentum uncertainty will decrease, resulting lower momentum, and lower kinetic energy. (uncertainty and absolute value are the same or not?)
- Delocalization could become covalent bond
- why delocalization lower K.E? I guess the probability curve between two protons become more smooth: then input the new wavefunction :we will get an smaller K.E term because the property of gradient square term in Hamiltonian !(smoother wave lower energy) always work:if the potential term get more important(charge goes up). the effect of delocalization maybe not enough!

$$T = \frac{p^2}{2m} = \frac{h^2}{2m\lambda^2} .$$

Using Particle in a box

Consider the one-dimension particle in a box.

$$V(x) = \begin{cases} 0, & 0 < x < L \\ \infty, & \text{otherwise} \end{cases}, \quad \begin{array}{l} \because \text{potential energy, } V(x) = 0 \\ \therefore \text{We only need to consider the kinetic energy.} \end{array}$$

$$\therefore \psi(x) = \sqrt{\frac{2}{L}} \cdot \sin\left(\frac{n\pi}{L}x\right), \quad E_n = \frac{n^2 h^2}{8mL^2}$$

Thus, as L increases \Rightarrow more delocalized $\Rightarrow E$ decreases
 \Rightarrow kinetic energy decreases.

Delocalization and Kinetic Energy

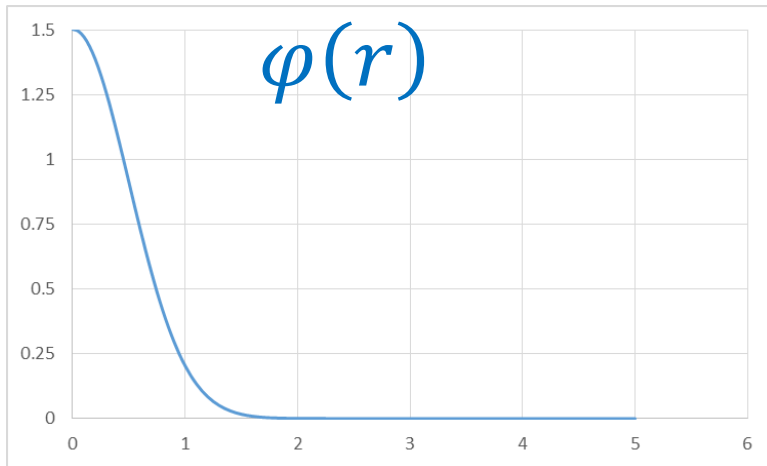
$$\hat{T} = -\frac{\hbar}{2m} \frac{d^2}{dr^2}$$

Kinetic energy is the average of the second derivative

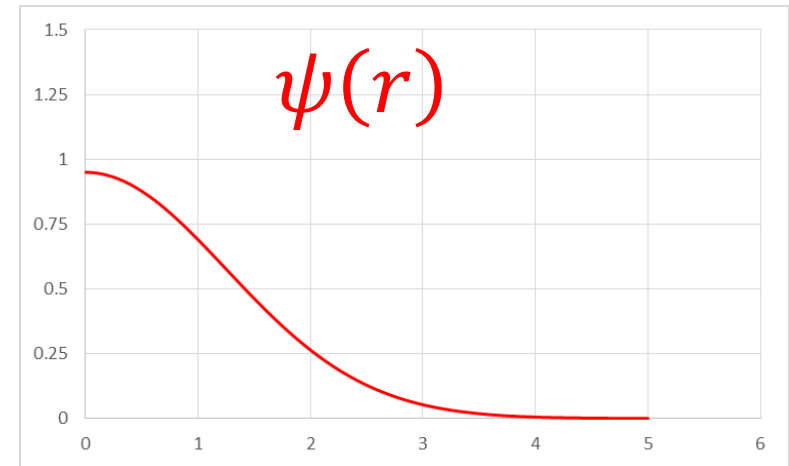
$$\hat{P} = i\hbar \frac{d}{dr}$$

Momentum is the average of the derivative

de broglé's relation $p = \frac{h}{\lambda}$ where λ is wavelength



Localized

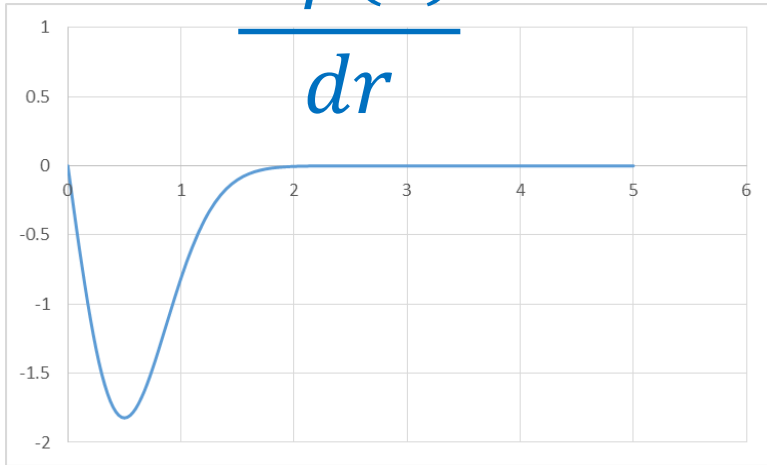


Delocalized

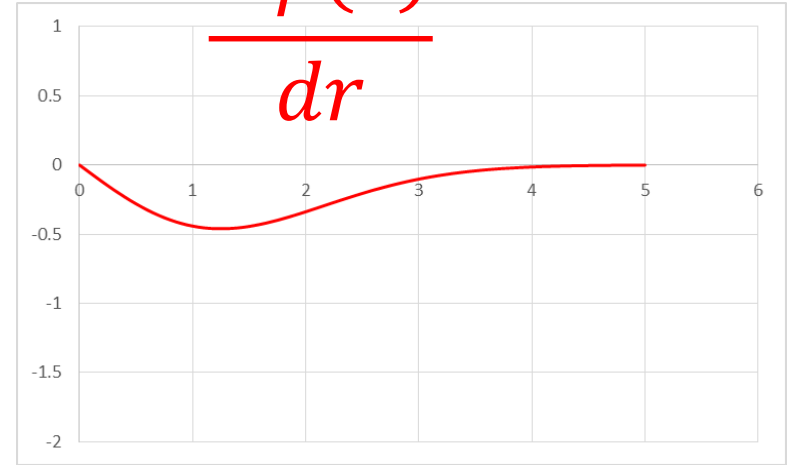
Area have to be kept same so what happens to the wavefunction?

Delocalization and Kinetic Energy 2

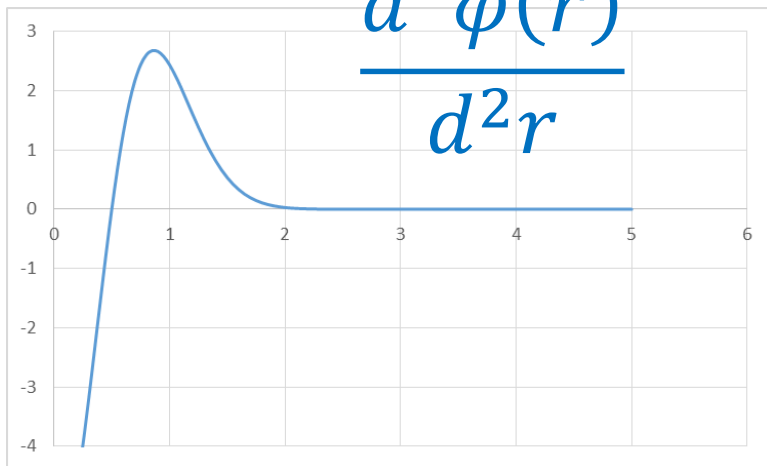
$d\varphi(r)$ Localized



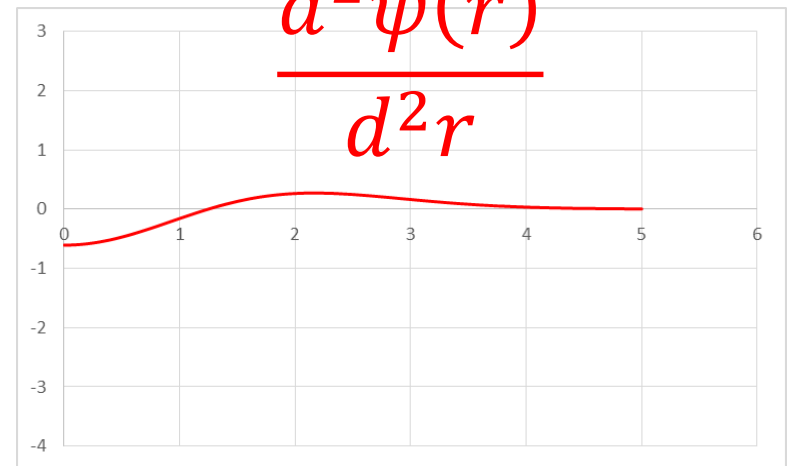
$d\psi(r)$ Delocalized



$\frac{d^2\varphi(r)}{d^2r}$



$\frac{d^2\psi(r)}{d^2r}$



$$-\int \varphi(r) \frac{d^2\varphi(r)}{d^2r} dr = 2.2$$

$$-\int \psi(r) \frac{d^2\psi(r)}{d^2r} dr = 0.33$$

Additional Orbitals

TABLE 10.2

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ϕ	E_{\min}/E_h	R_{eq}/a_0
$1s(\zeta = 1.000)$ Larger coefficient means	-0.564 83	2.49
$1s(\zeta = 1.238)$ smaller orbital	-0.586 51	2.00
$1s(\zeta = 1.000) + a2p_z(\zeta = 1.000)$	-0.565 91	2.00
$1s(\zeta = 1.247) + b2p_z(\zeta = 1.247)$	-0.599 07	2.00
$1s(\zeta = 1.2458) + c2p_z(\zeta = 1.4224)$	-0.600 36	2.00
$1s(\zeta = 1.244) + c_1 2p_z(\zeta = 1.152) + c_2 3d_{z^2}(\zeta = 1.333)$ ^b	-0.6020	2.00
Exact ^c	-0.602 64	2.00

^a The molecular orbitals are of the form $\psi_b = c_A \phi_A + c_B \phi_B$, where ϕ is given in the table.

^b Mulliken, R. S., Ermler, W. C. *Diatomic Molecules*. Academic Press: New York, 1977.

^c Bates, D. R., Ledsham, K., Stewart, A. L. Wave Functions of the Hydrogen Molecular Ion. *Philos. Trans. Roy. Soc. London, Ser. A.* **246**, 215 (1953).

Why Smaller Orbital Helps

- 2. A larger atom has more electrons and orbitals, and more coupling between orbitals, which are too complicated to use the approximation.

2: why a smaller wave function help? the electron get closer to proton: potential decrease ; thought the faster decreasing exponential term means higher K.E. just opposed to the effect of the first question ! (how can we do that? what's the meaning of parameter?)

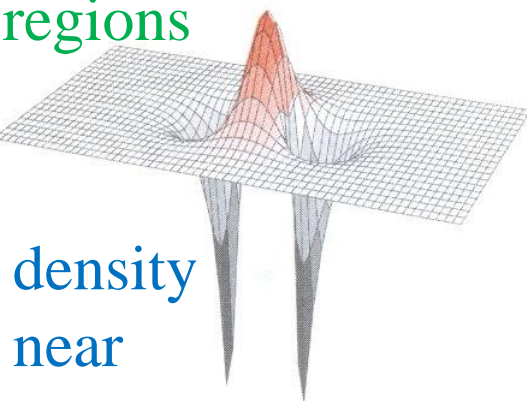
The smaller atomic wavefunction means the higher effective charge. (i.e. the term in wavefunction $e^{-Z_{\text{eff}}r/a_0}; e^{-1r/a_0} \rightarrow e^{-1.238r/a_0}$). The higher effective charge is natural for our physical intuition since that the electron faces two nucleus rather than

Using smaller Orbitals

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Larger coefficient means
smaller orbital

Growth of density at
interatomic regions

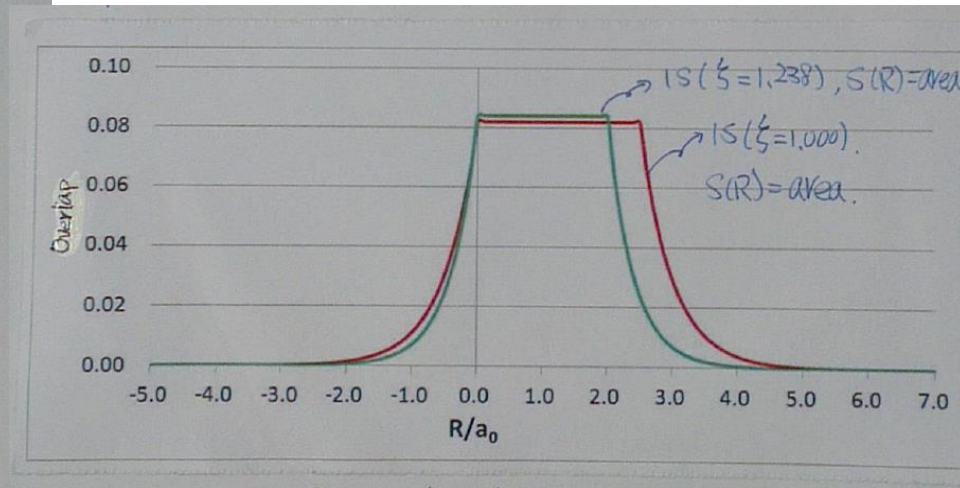
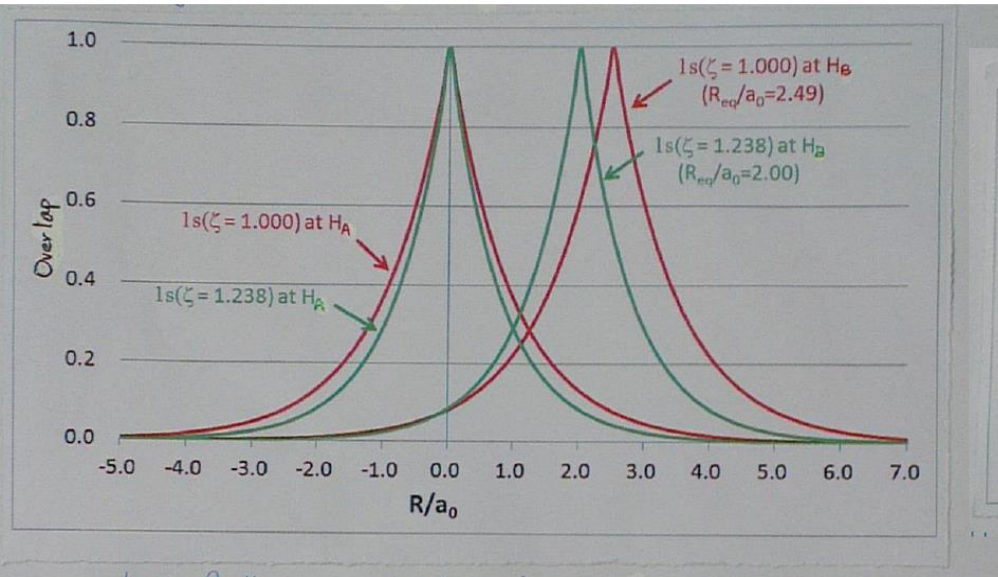
Decrease of density
from region near
nucleus

Bonding Orbital

The bonding orbital
has sharper structure
near the nuclei

Better described by a
smaller coefficient

Look at what happens with smaller orbital



① When $1s(\zeta = 1.238)$ and $R_{eq}/a_0 = 2.00$, $S_1 = 0.237$

② When $1s(\zeta = 1.000)$ and $R_{eq}/a_0 = 2.49$, $S_2 = 0.288$.

For $\bar{E}_+(R) = \frac{H(R)_{AA} + H(R)_{AB}}{1 + S(R)}$

Energy level diagram for H_2^+ molecular ion. The diagram shows the energy levels of the two hydrogen atoms and the resulting molecular ion energy levels. The atomic energy levels are labeled ϕ_A and ϕ_B with energy E_{1s} . The molecular ion energy levels are labeled ψ_+ and ψ_- with energy E_+ and E_- respectively. The energy levels are shown as dashed lines, indicating the interaction between the atomic orbitals.

Why 2P orbital helps but 2S does not 1

- 3: why adding 2p but 2s is useful? because different type of orbital can hybrid to lower energy. 1s and 2s are orthogonal so adding 2s is useless! (hybrid is not enough, we need to shirk the orbital using parameter)
1s and 2p are also orthogonal
- 3.2p orbital is more "orthogonal" to 1s orbital than 2s orbital is to 1s orbital.

Why 2P orbital helps but 2S does not 2

calculation, we never consider the angular contribution. According to quantum mechanics, s-orbit is spherical symmetry, while p-orbit is cylindrical symmetry. From the view of the electron, considering Born-Oppenheimer approximation (i.e. regard the nucleus is moving much slower than electron or say almost fixed at some place), it sees two nucleus lying on an axis; therefore, the potential due to this two nucleus should be cylindrical symmetry. The angular parts do contribute to the calculation! 2p seems to be more appropriate to describe the H_2^+ system. Thus, only considering spherical symmetry- s-orbit, may not give the correct result even adding the contribution of different principle quantum number. That is the reason why adding 2p can increase more accuracy than 2s.

Using $2p_z$ Orbitals Hand waving

$1s(\zeta = 1.000)$

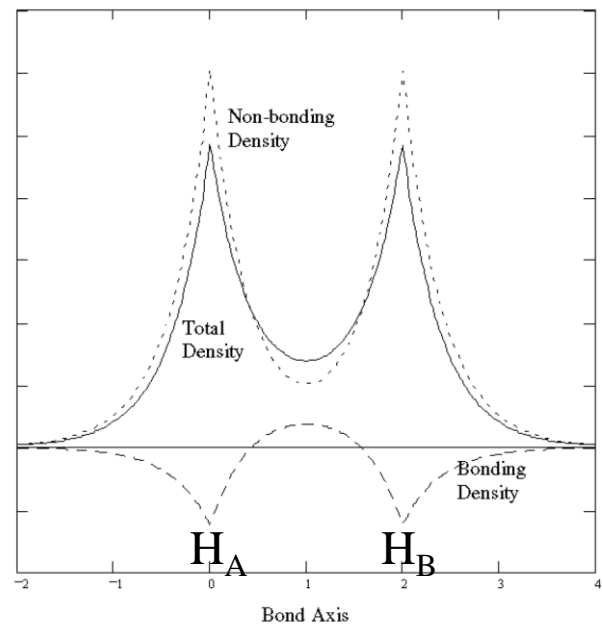
-0.564 83 2.49

$1s(\zeta = 1.238)$

-0.586 51 2.00

$1s(\zeta)$

-0.565 91 2.00

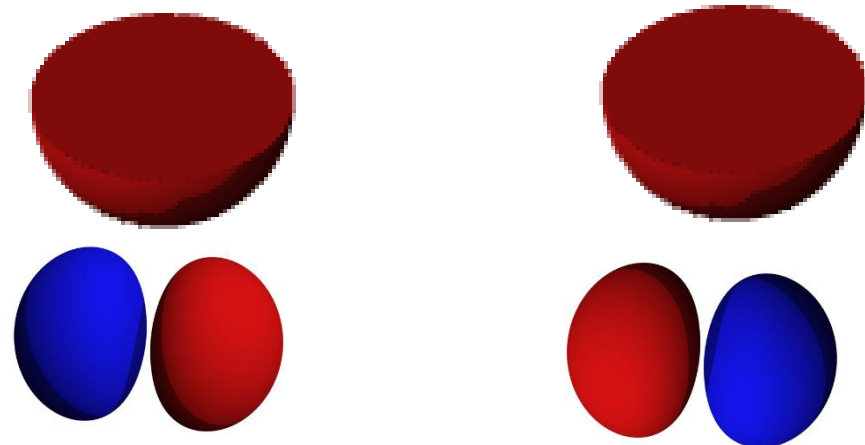


Bonding Orbital

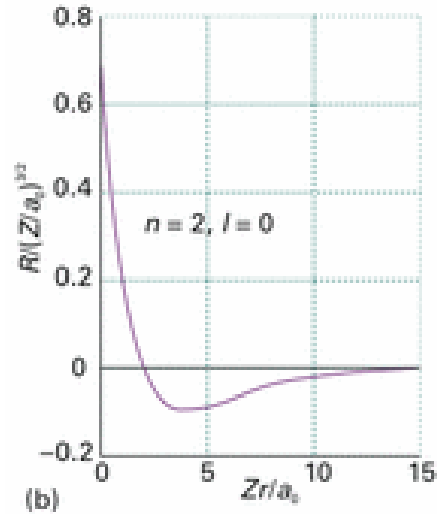
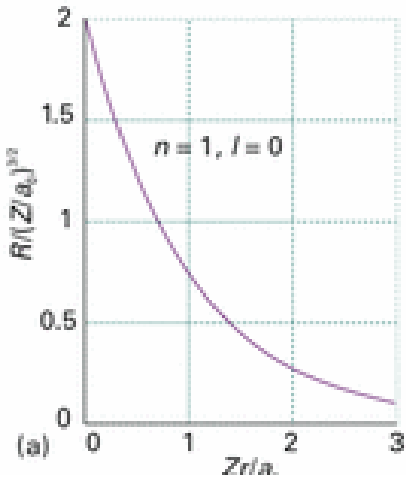
The bonding orbital has asymmetric distribution around nuclei

Better described by a $2p_z$ orbital

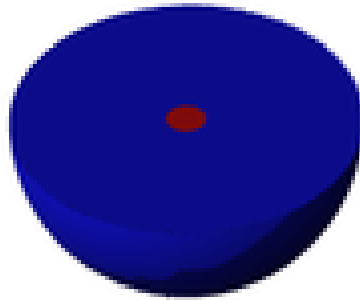
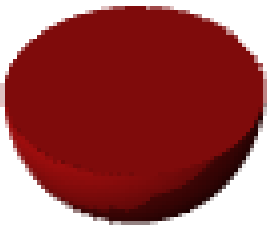
Polarization orbital!



Addition of 2S Orbitals what will it do?



2s orbitals are much bigger than the 1s orbital, but it is still symmetric around the H atom center



Basis Set

- If you use more atomic orbitals to define the molecular orbital usually the energy gets closer to the exact solution

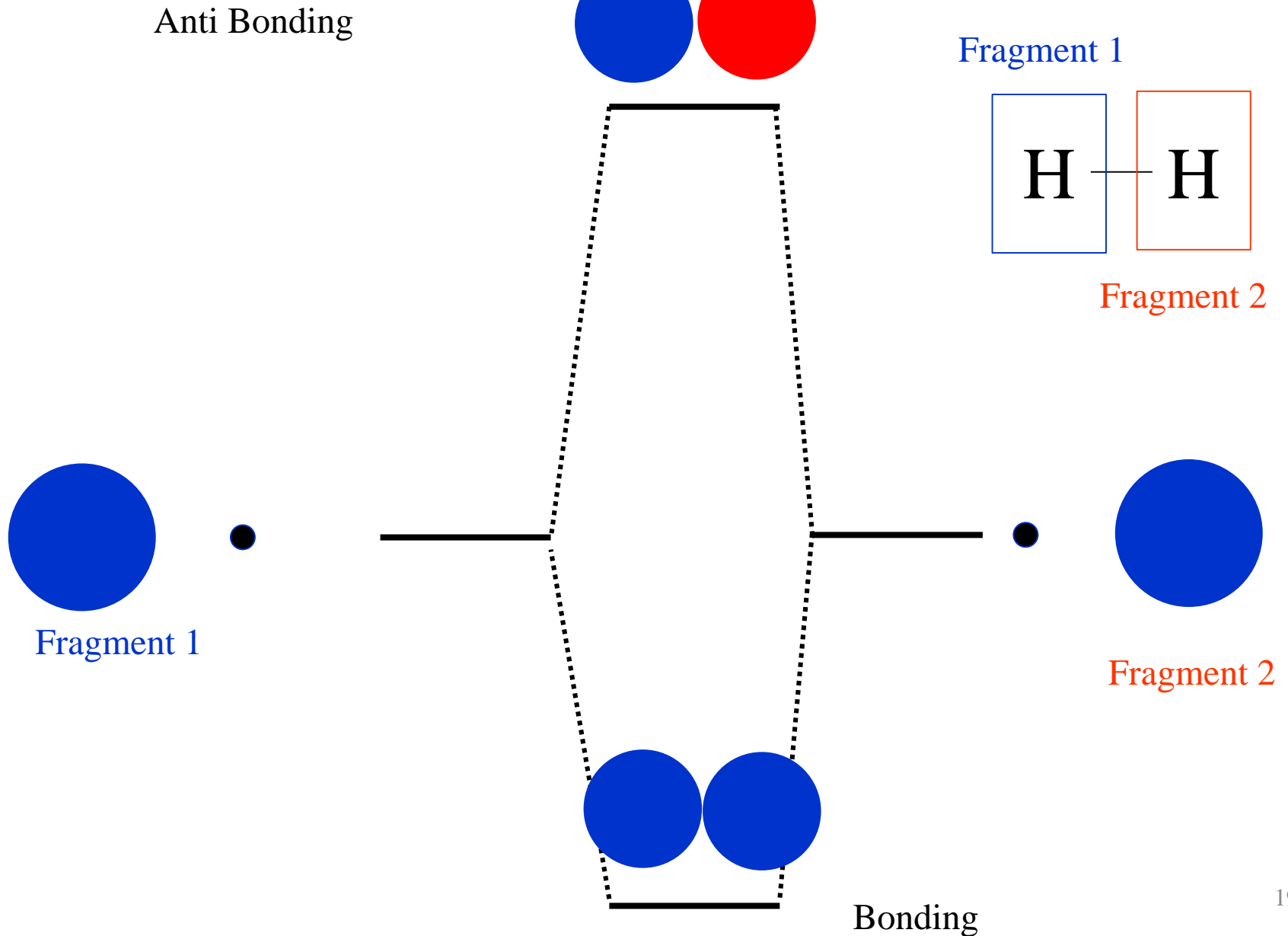


Using a bigger basis set to describe the system

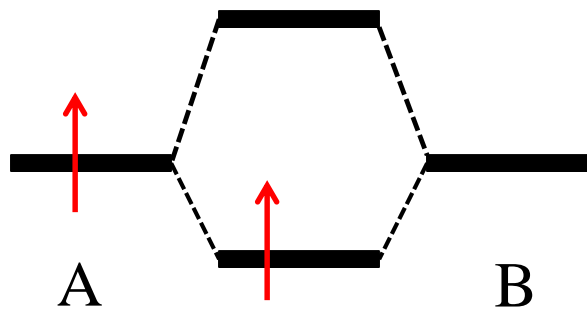
- However bigger basis set you need more time to calculate.
- Changing coefficient on basis set is also important

Diatomic Molecules Chemist's view

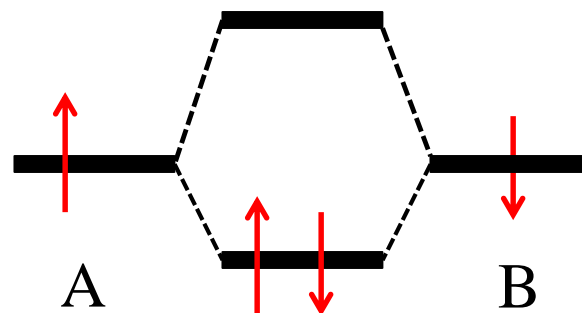
Linear H₂



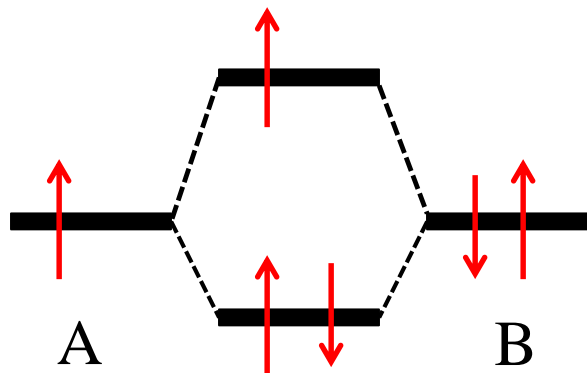
H_2^+ , H_2 , He_2^+ , He_2



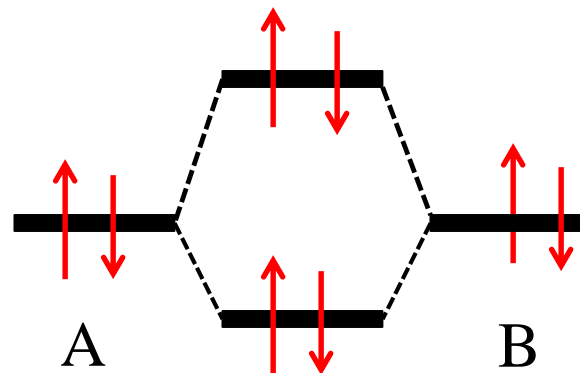
H_2^+ $R_{eq}=1.06$ Angstrom
Binding Energy 61 kcal/mol



H_2 $R_{eq}=0.74$ Angstrom
Binding Energy 105 kcal/mol



He_2^+ $R_{eq}=1.08$ Angstrom
Binding Energy 50 kcal/mol

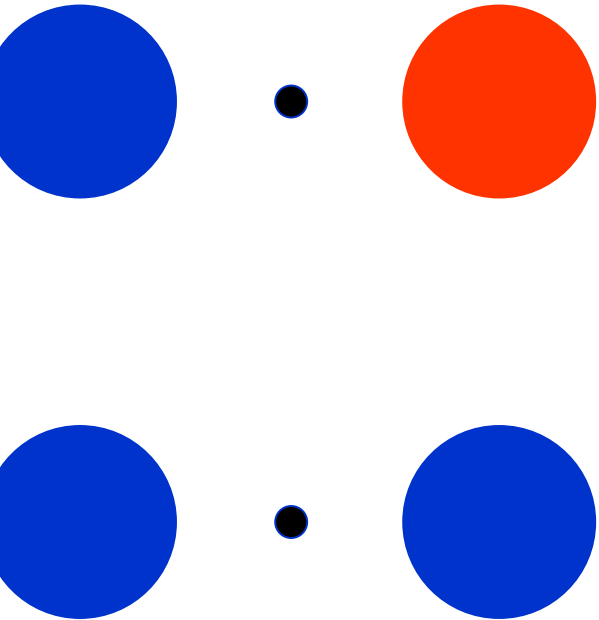
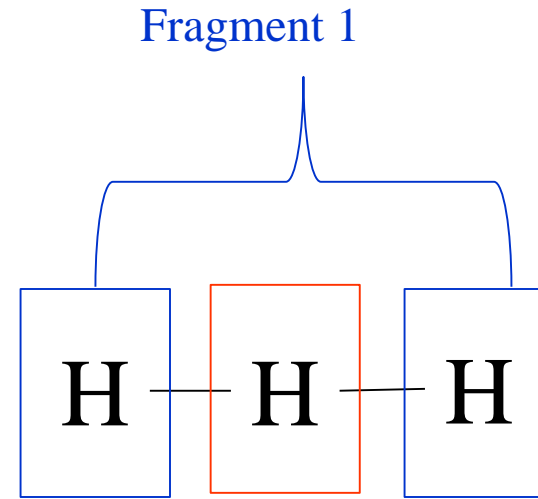
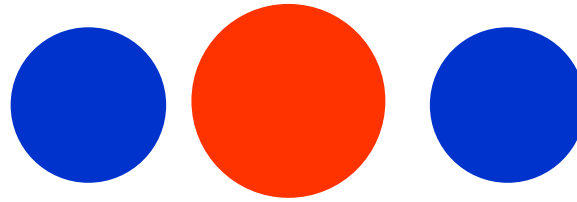


He_2 $R_{eq}=$ Infinity not bound
Binding Energy 0 Kcal mol

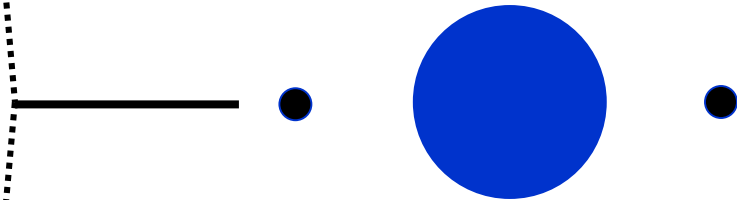
Polyatomic Molecules

Linear H₃

Anti Bonding

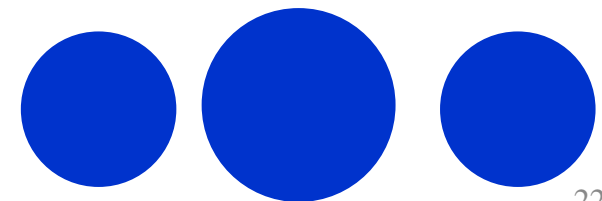


Non Bonding
stays the same



Fragment 2

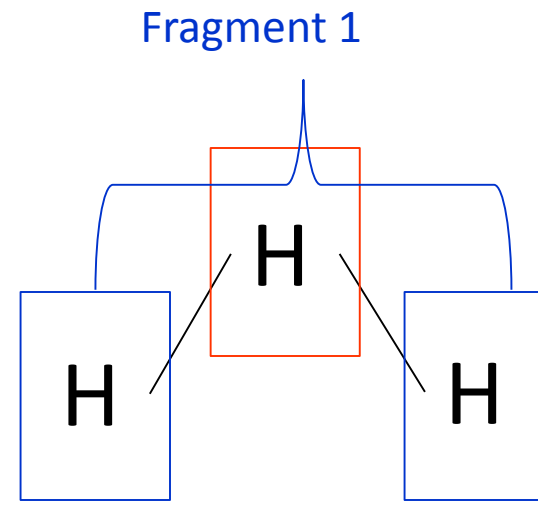
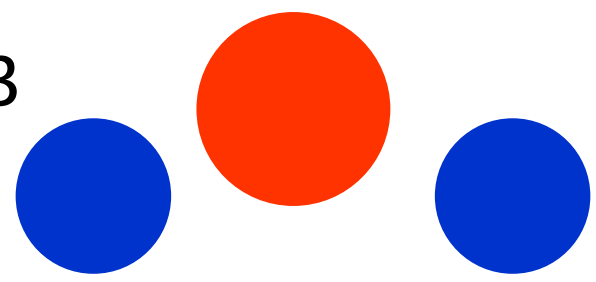
Fragment 1



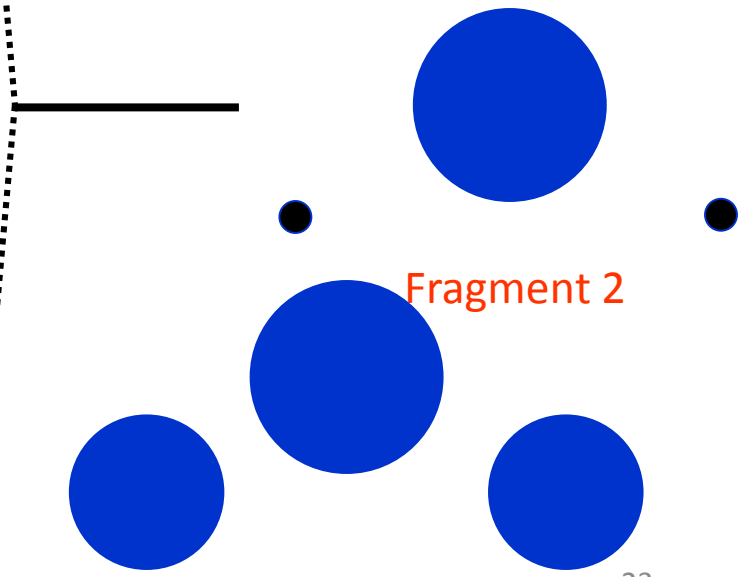
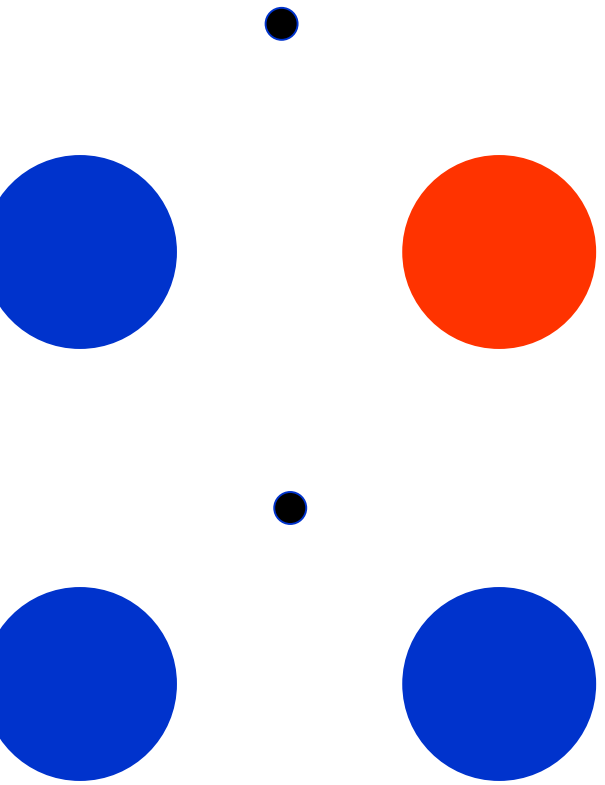
Bonding

Triangle H₃

Anti Bonding



Non Bonding



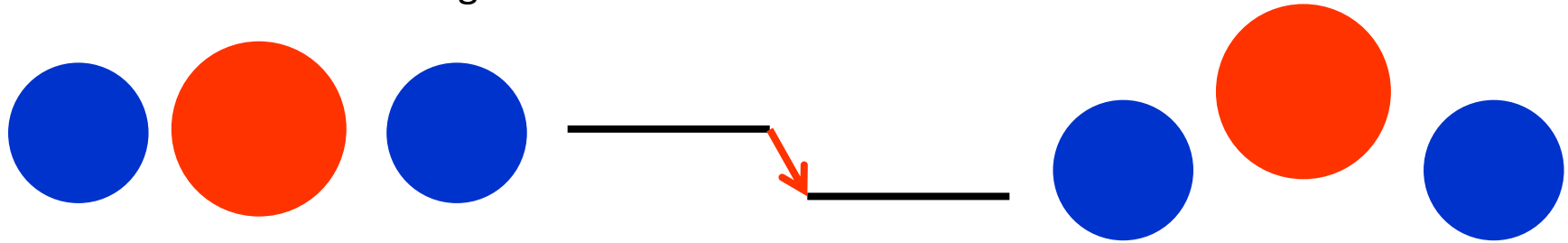
Fragment 1

Bonding

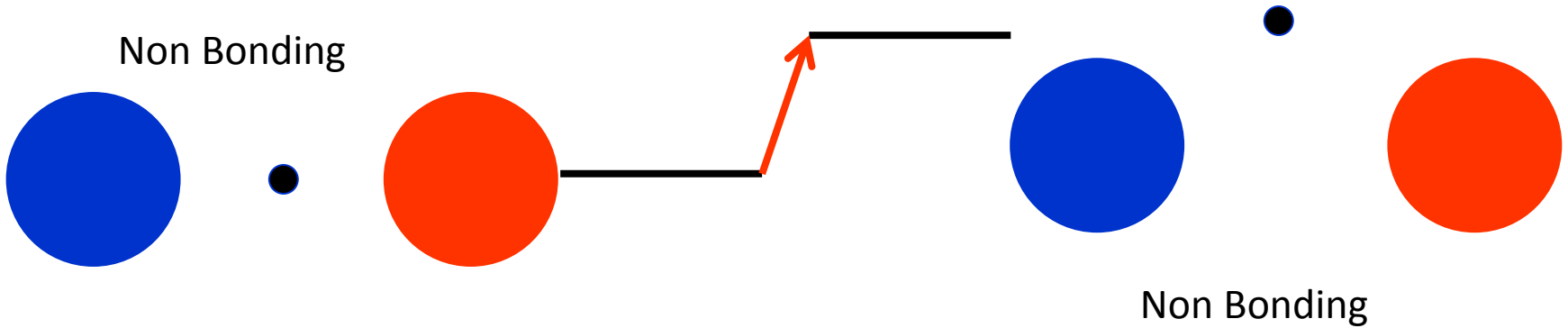
Fragment 2

Linear H₃ vs Triangular H₃

Anti Bonding

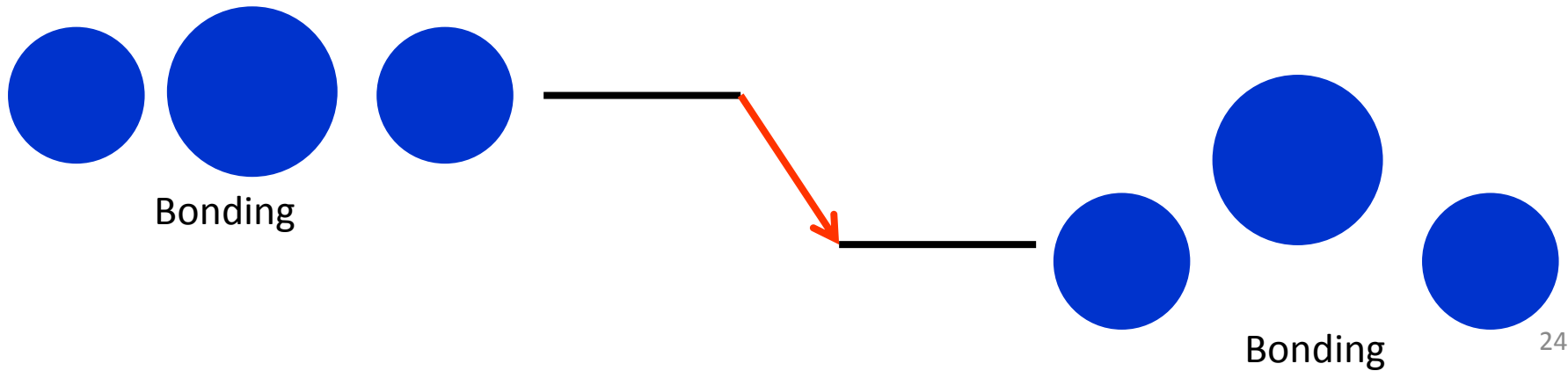


Non Bonding



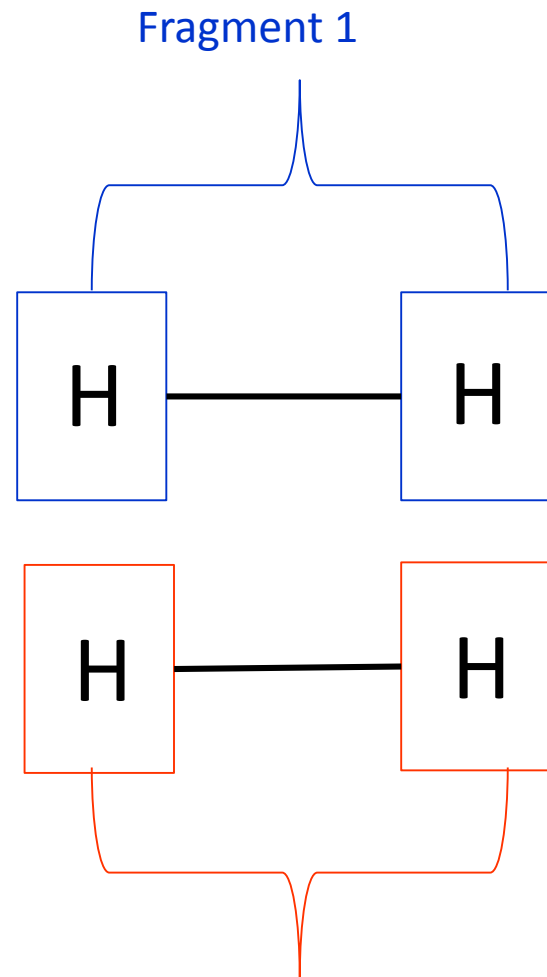
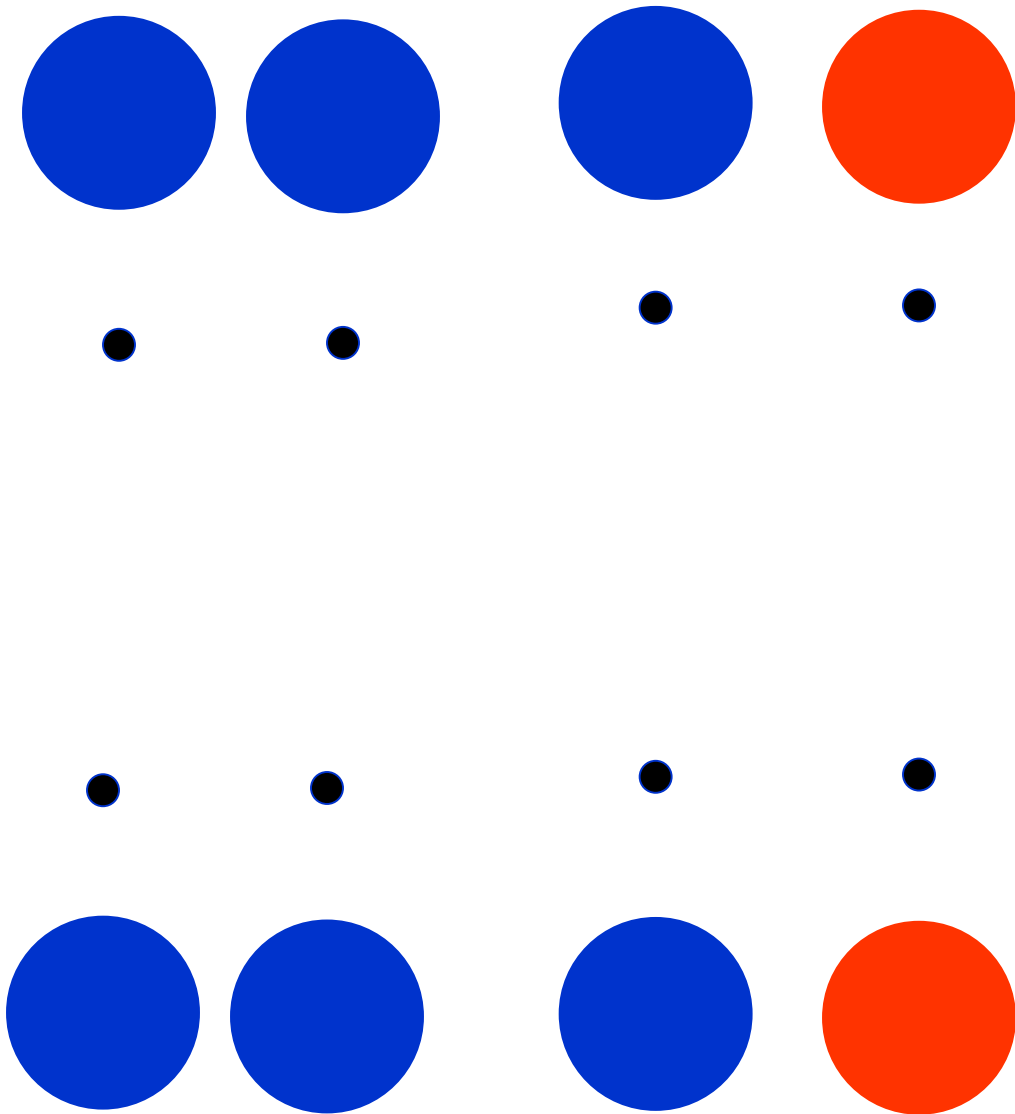
Non Bonding

Bonding



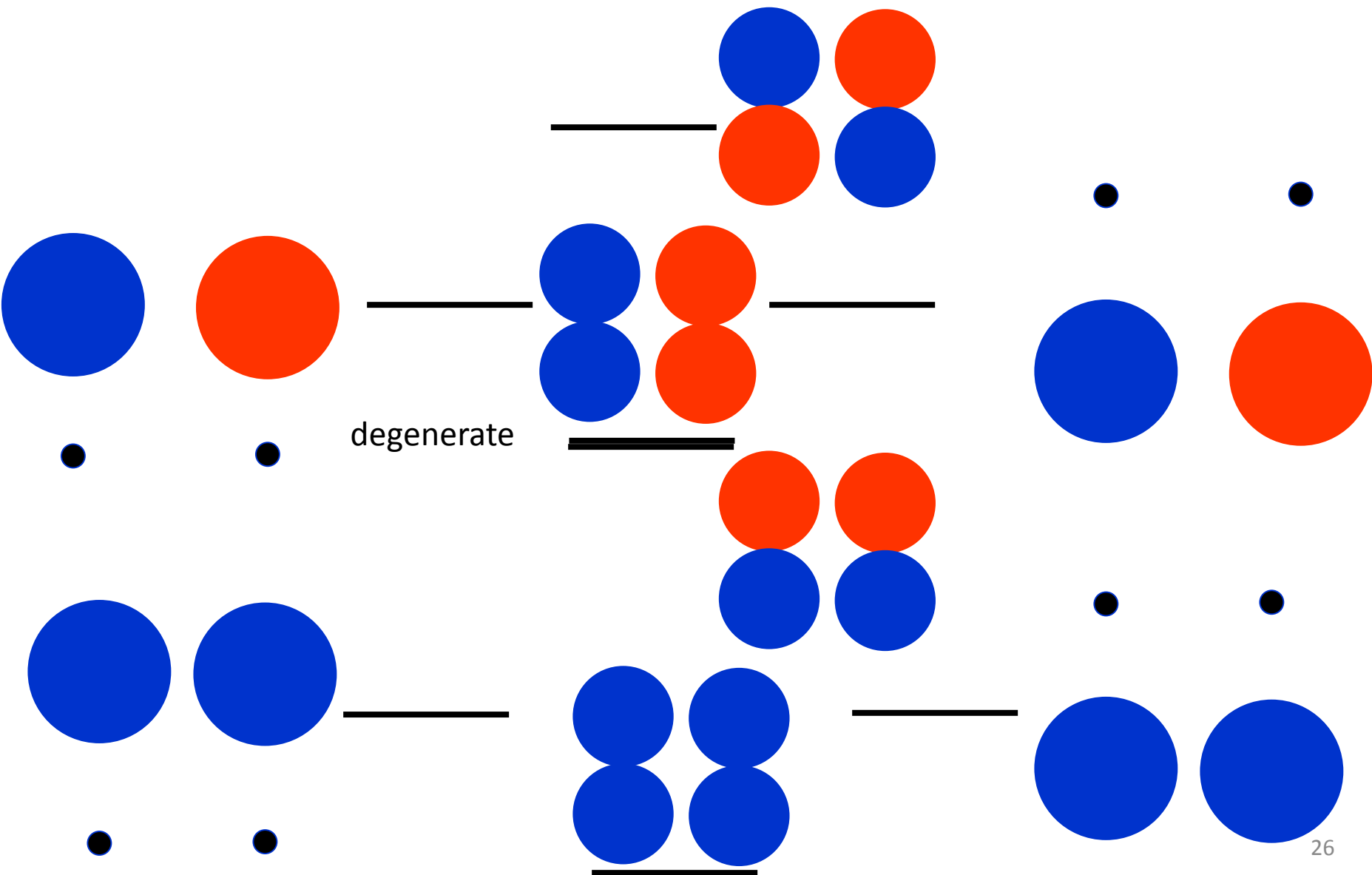
Bonding

H₄ Square

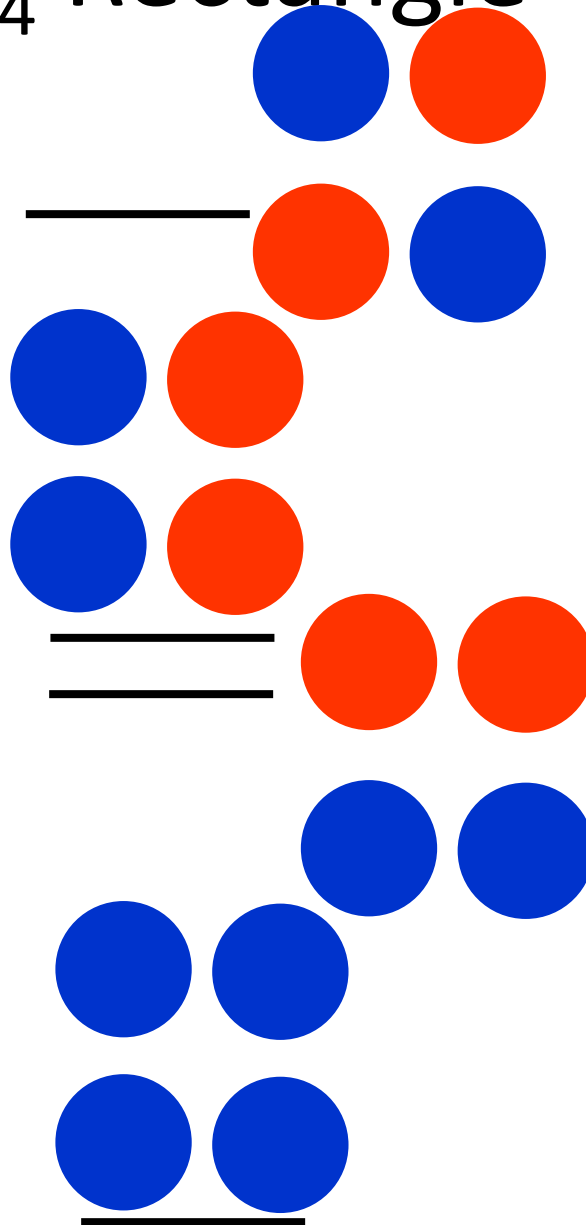


Fragment 2

H₄ square

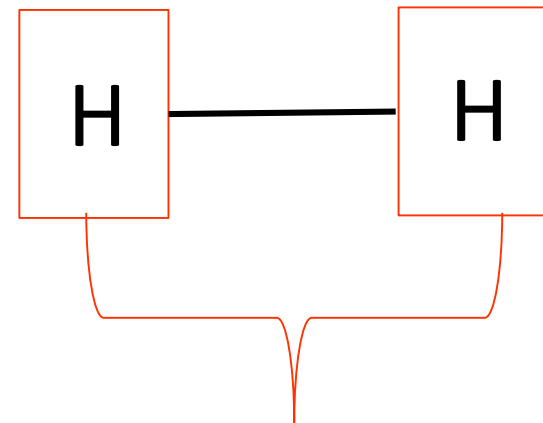
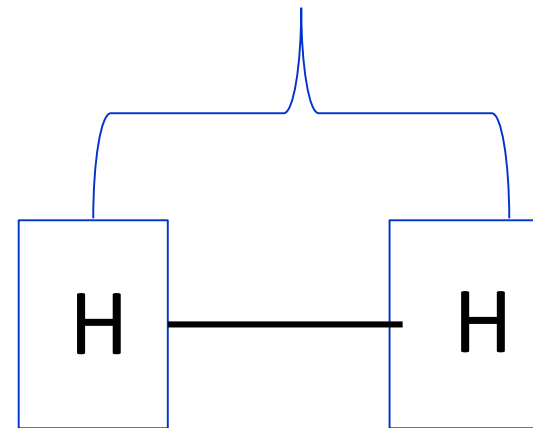


H₄ Rectangle



Degenerate orbitals split!

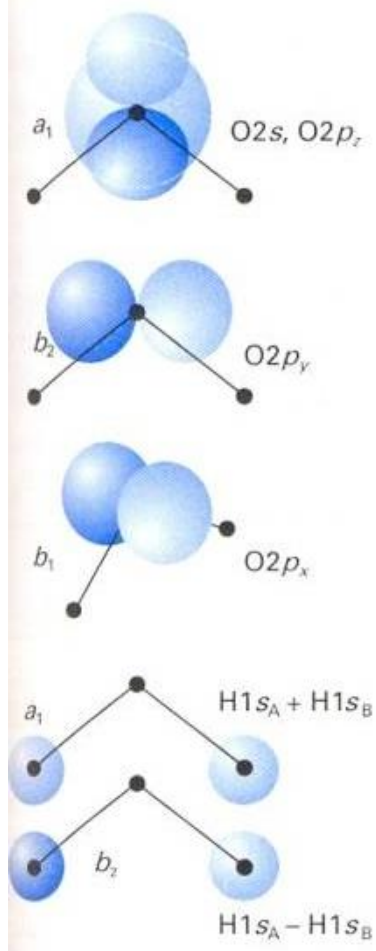
Fragment 1



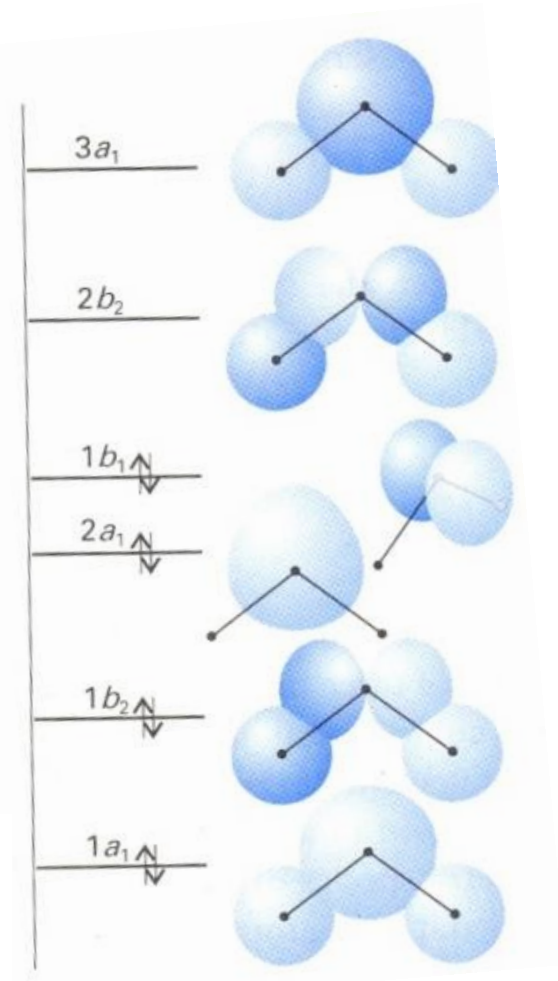
Fragment 2

Water H₂O

You must think of symmetry:
 Rotation of bisector axis
 Mirror at the water plane
 Mirror at the middle



Hydrogens make linear combination: plus and minus pair like bonding and antibonding orbital

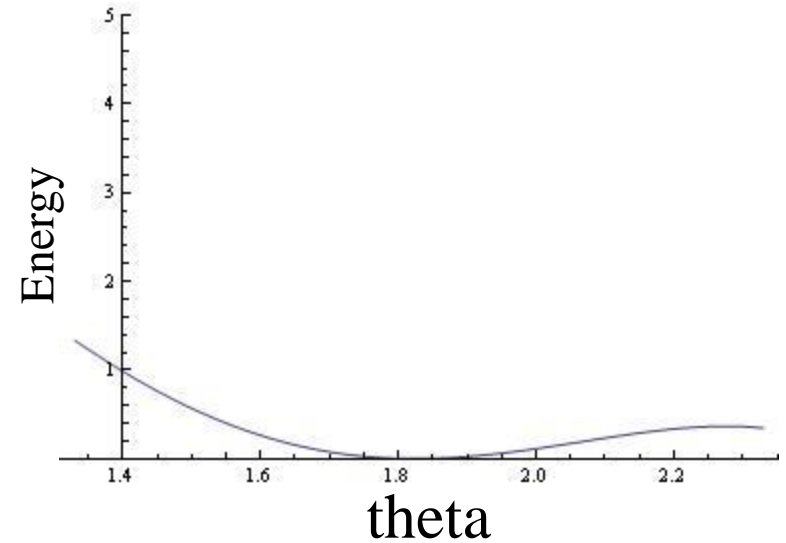
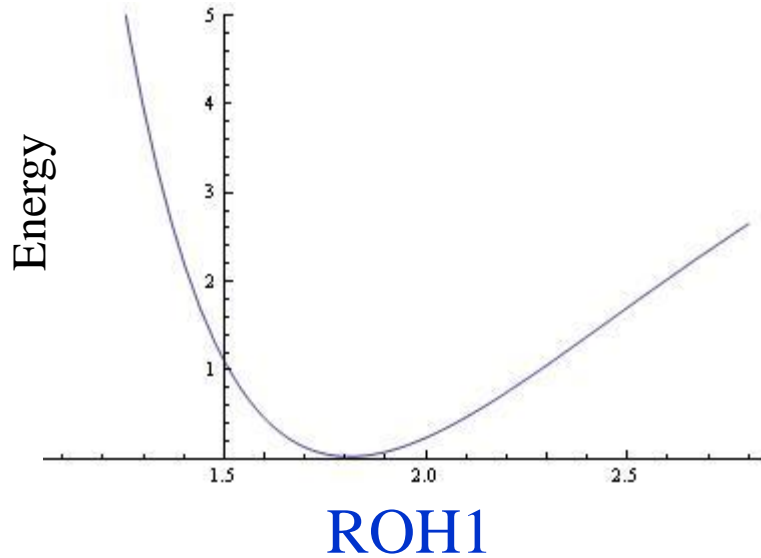
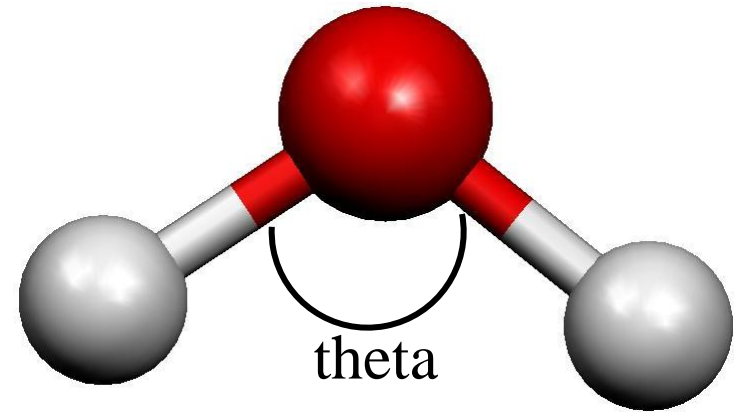
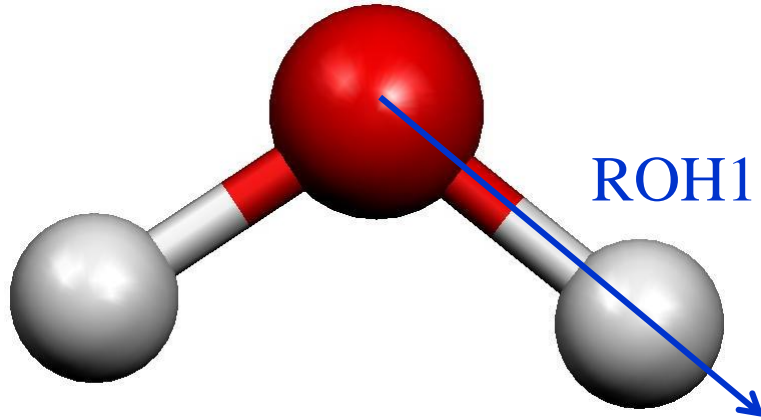


C_{2v}	O ₂ s	O ₂ p _x	O ₂ p _y	O ₂ p _z	H1s _A	H1s _B
E	O ₂ s	O ₂ p _x	O ₂ p _y	O ₂ p _z	H1s _A	H1s _B
C_2	O ₂ s	-O ₂ p _x	-O ₂ p _y	O ₂ p _z	H1s _B	H1s _A
σ_v	O ₂ s	O ₂ p _x	-O ₂ p _y	O ₂ p _z	H1s _B	H1s _A
σ'_v	O ₂ s	-O ₂ p _x	O ₂ p _y	O ₂ p _z	H1s _A	H1s _B

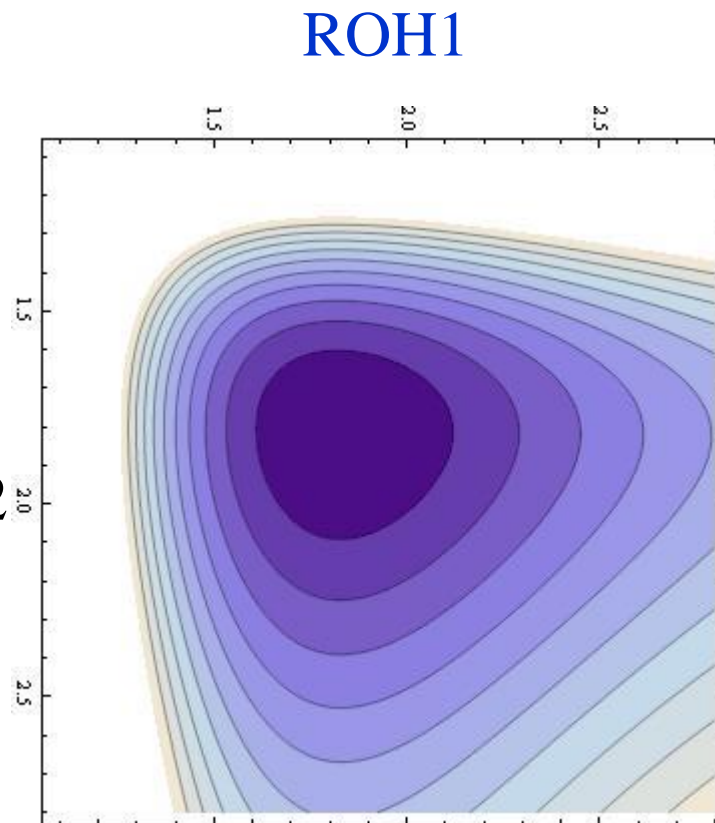
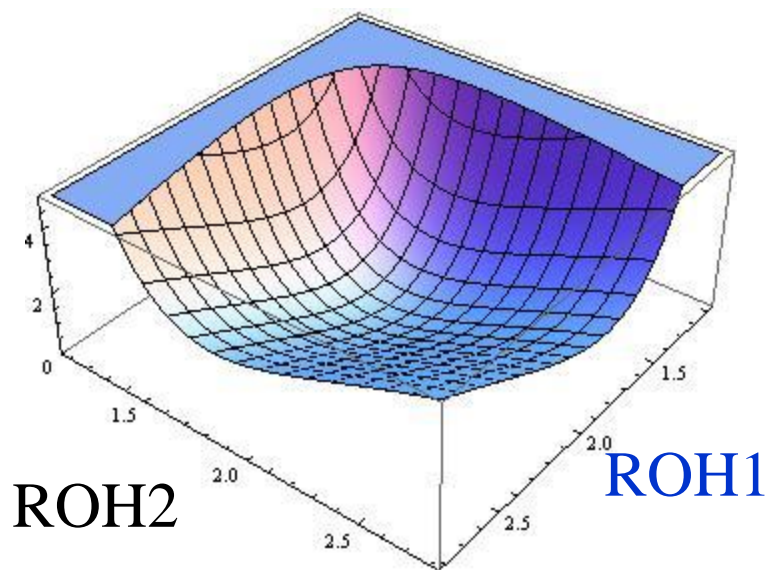
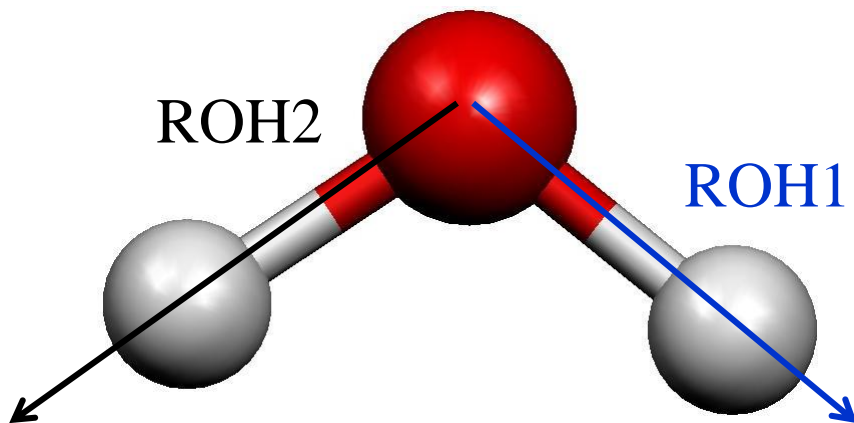
Potential Energy Surface Reaction

Kaito Takahashi

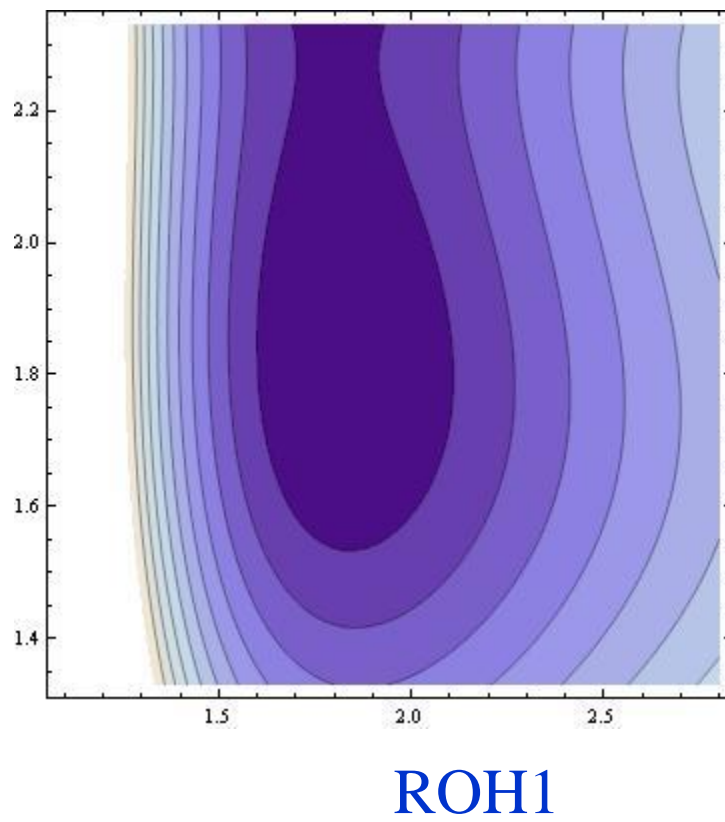
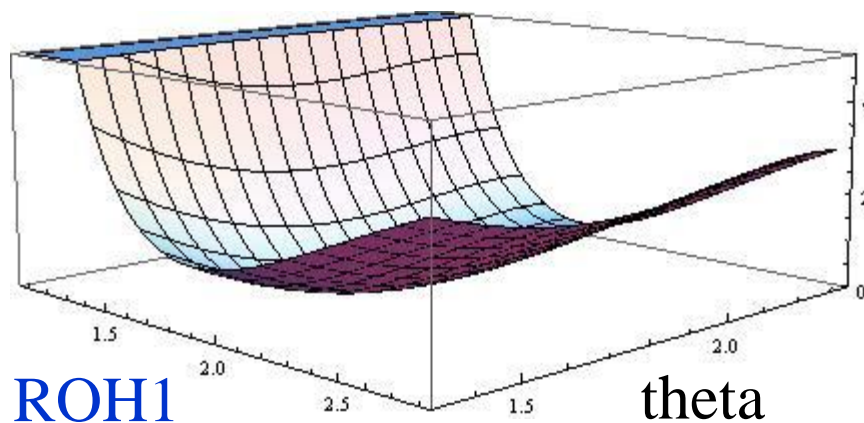
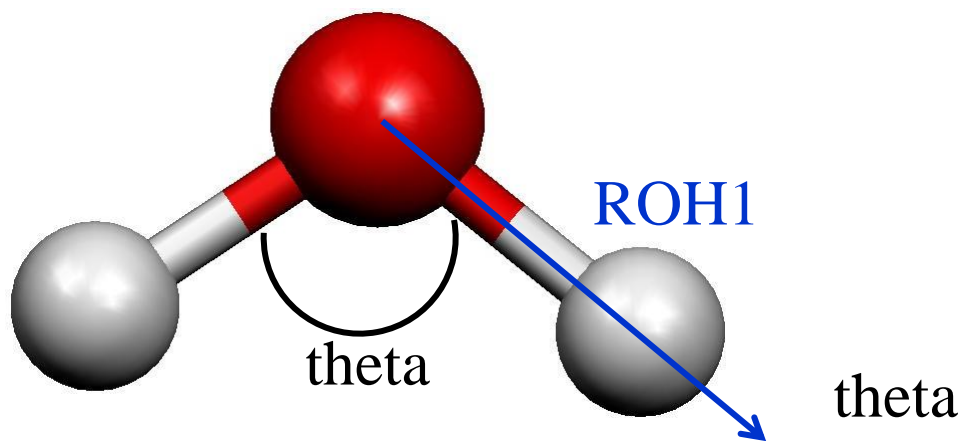
Water Molecule Potential Energy Curve



Water Molecule: Stretch Stretch Potential Energy Surface



Water Molecule: Stretch Bend Potential Energy Surface



Vibration

Potential Energy Curve

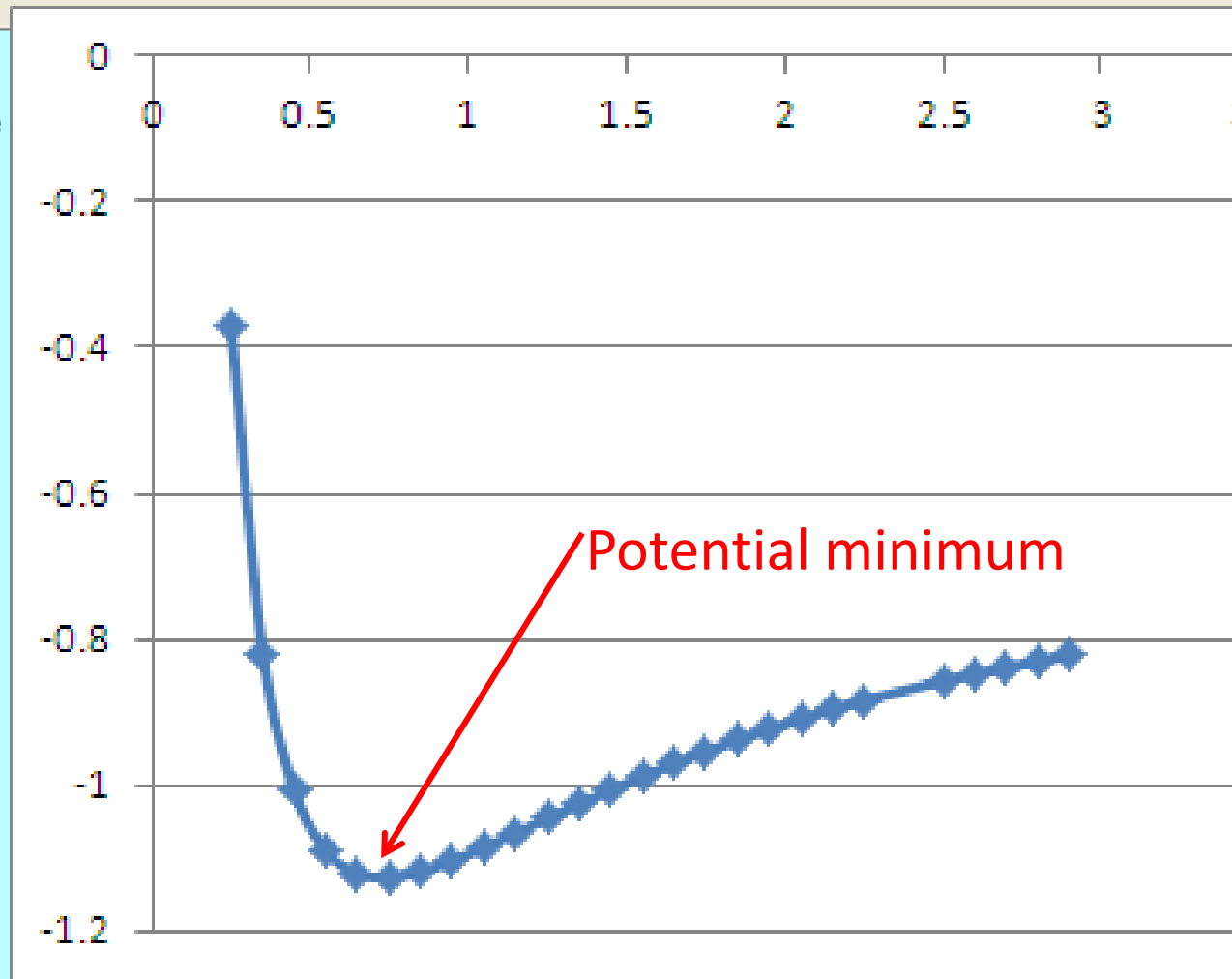
140.109.112.238:22 - Tera Term VT

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Scan completed.

Summary of the potential surface

N	RH1H2	SCF
1	0.2500	-0.37196
2	0.3500	-0.81916
3	0.4500	-1.00834
4	0.5500	-1.09016
5	0.6500	-1.12120
6	0.7500	-1.12655
7	0.8500	-1.11854
8	0.9500	-1.10365
9	1.0500	-1.08542
10	1.1500	-1.06576
11	1.2500	-1.04576
12	1.3500	-1.02600
13	1.4500	-1.00682
14	1.5500	-0.98838
15	1.6500	-0.97078
16	1.7500	-0.95407
17	1.8500	-0.93827
18	1.9500	-0.92338
19	2.0500	-0.90939
20	2.1500	-0.89628
21	2.2500	-0.88403



Leave Link 108 at Mon Mar 21 17:55:19 2011, MaxMem= 33554432 cpu: 0.0
h2scan.log lines 3718-3746/3766 99%

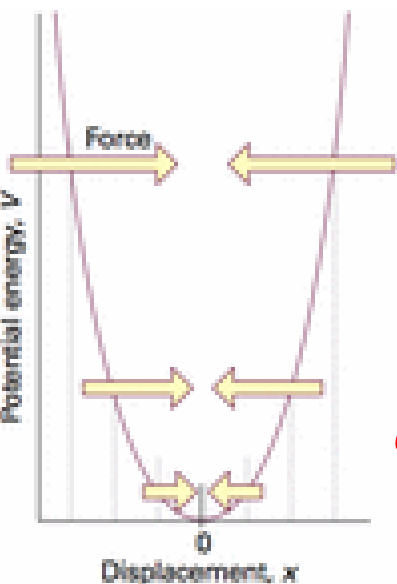
How to quantify Minimum?

- At the minimum the first derivative is zero and the second derivative is always positive

Check the Hessian (second derivative)

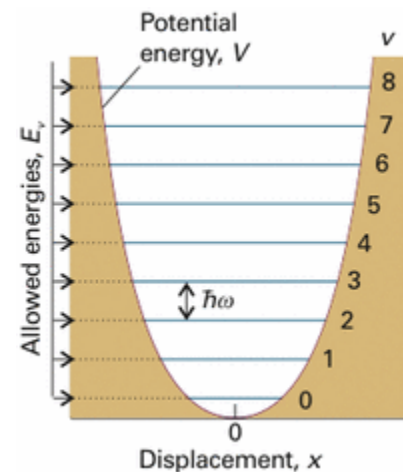
In Gaussian you can use the freq keyword

Harmonic Oscillator



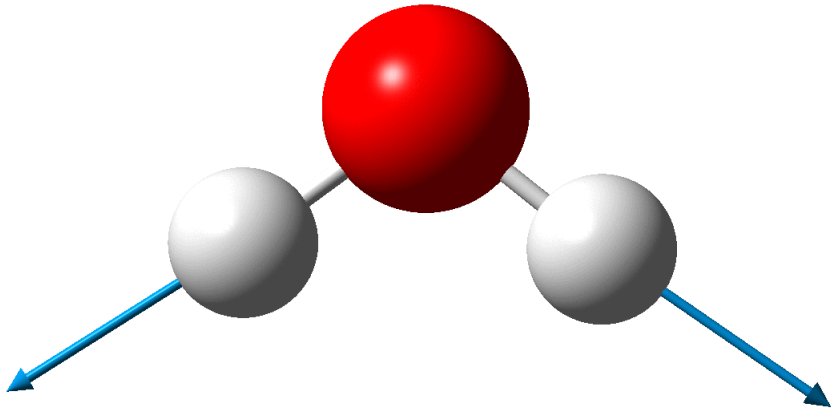
$$F = m \frac{d^2 x}{dt^2} = -kx \quad k: \text{force constant}$$

$$\omega = \sqrt{\frac{k}{m}} \quad E_n = \left(n + \frac{1}{2} \right) \hbar \omega \quad n = 0, 1, 2, \dots$$

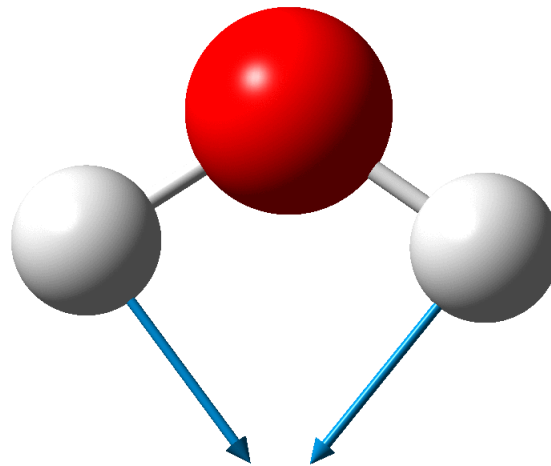
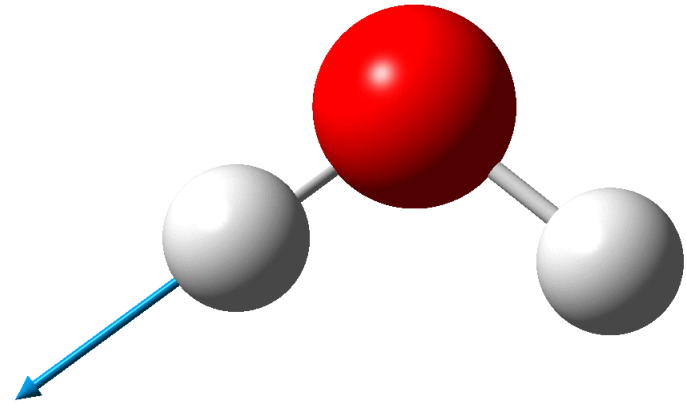


Normal Modes of Water

Symmetric stretch



Antisymmetric stretch

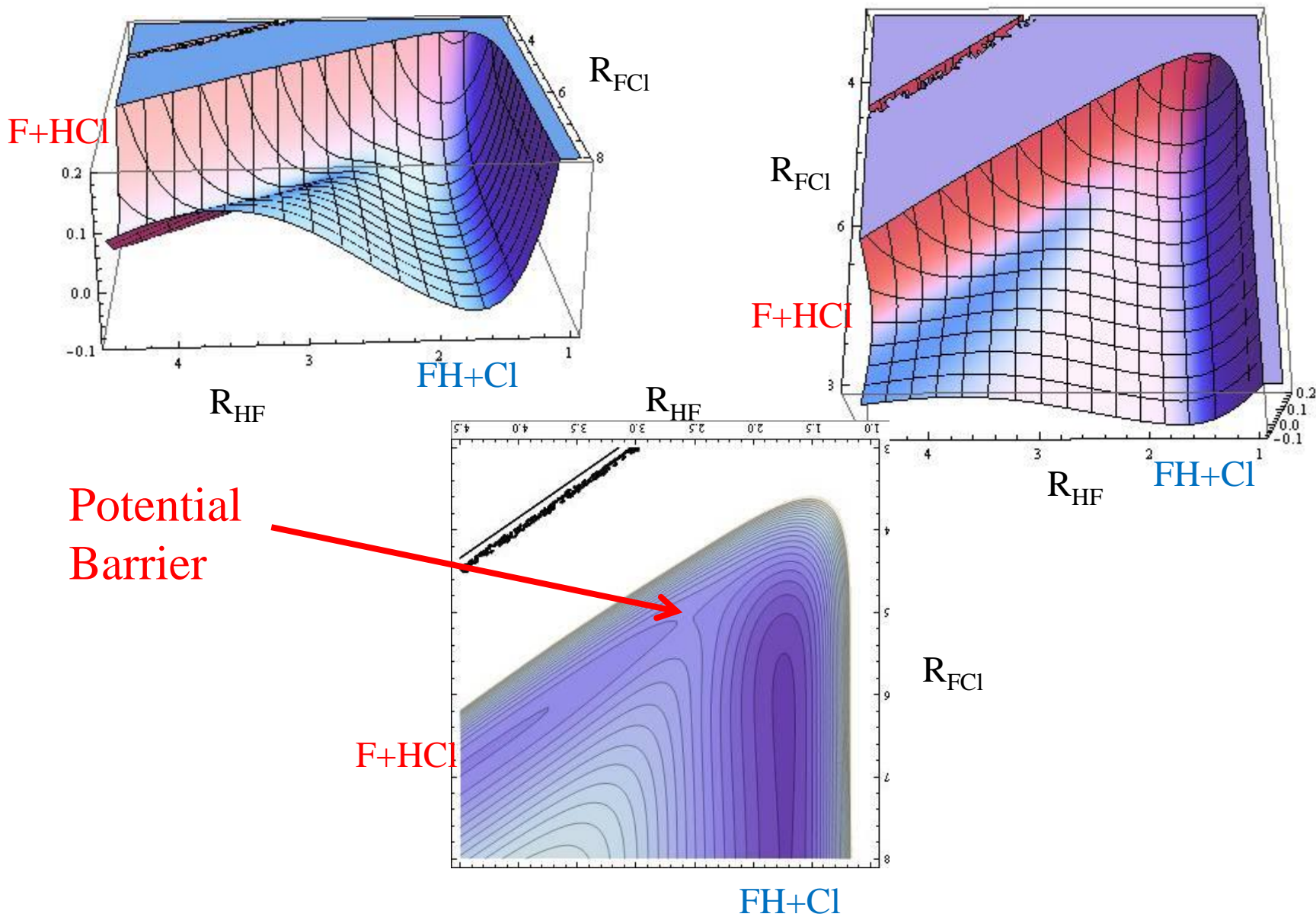


Bend

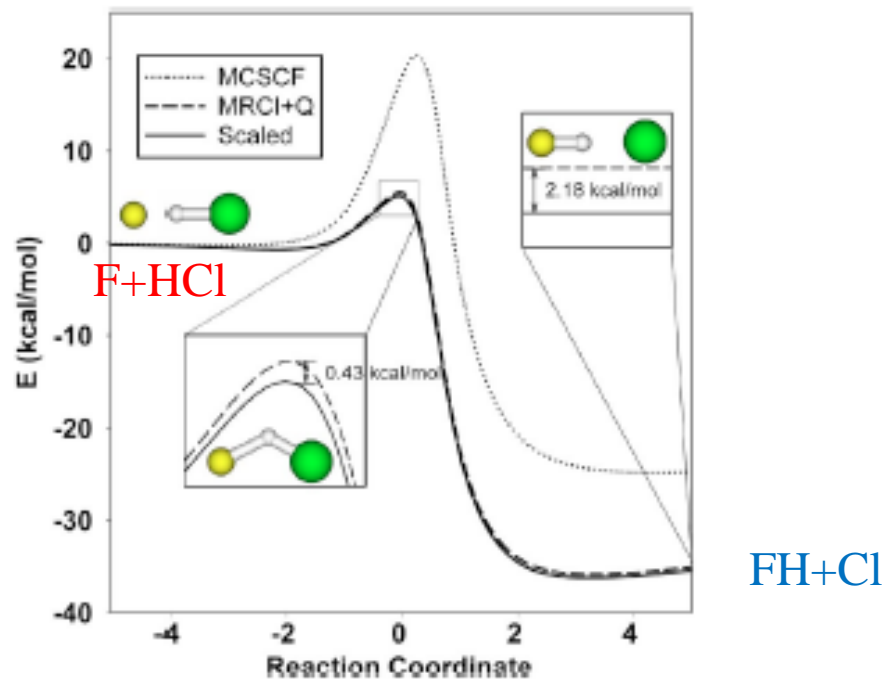
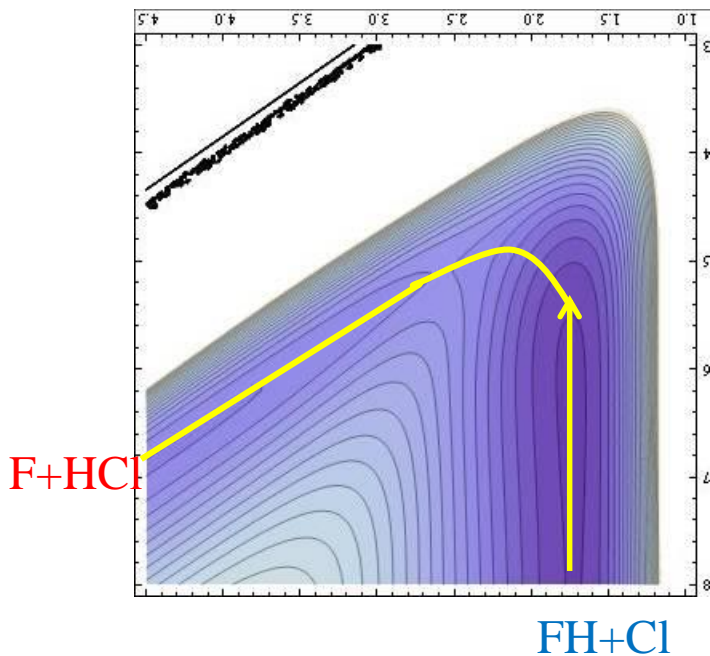
Reaction

F+HCl→FH+Cl Potential Energy Surface

Hydrogen Abstraction Reaction, break a HCl bond form a HF bond



Potential Energy Curve along IRC

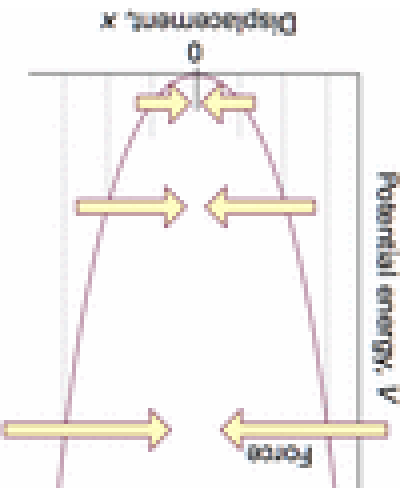


You need enough energy to go over the potential barrier to react!
The minimum energy path that connect the barrier with reactant and product is called intrinsic reaction path
For F+HCl case you need about 5 kcal/mol of for reaction to occur

How to quantify Barrier?

- At the barrier the first derivative is zero and the second derivative is negative for one degree of freedom and the rest are always positive. In Gaussian you can use the freq keyword to check if there is imaginary frequency

Harmonic Oscillator approximation at barrier

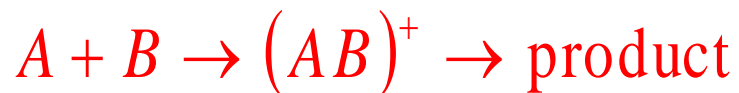


$$F = m \frac{d^2 x}{dt^2} = -kx \quad k: \text{force constant} \quad \omega = \sqrt{\frac{-k}{m}}$$

In the case of barrier the force constant k is negative
so omega is imaginary

Transition State Theory

- Once you have the barrier you can estimate the thermal rate constant of the reaction from the calculation results! (Assuming that the reaction proceeds along the IRC)



Activated Complex
(Geometry at Potential Barrier)

$$-\left(\frac{d[A]}{dt}\right) = \frac{k_B T}{h} K^{\ddagger} [A][B]$$

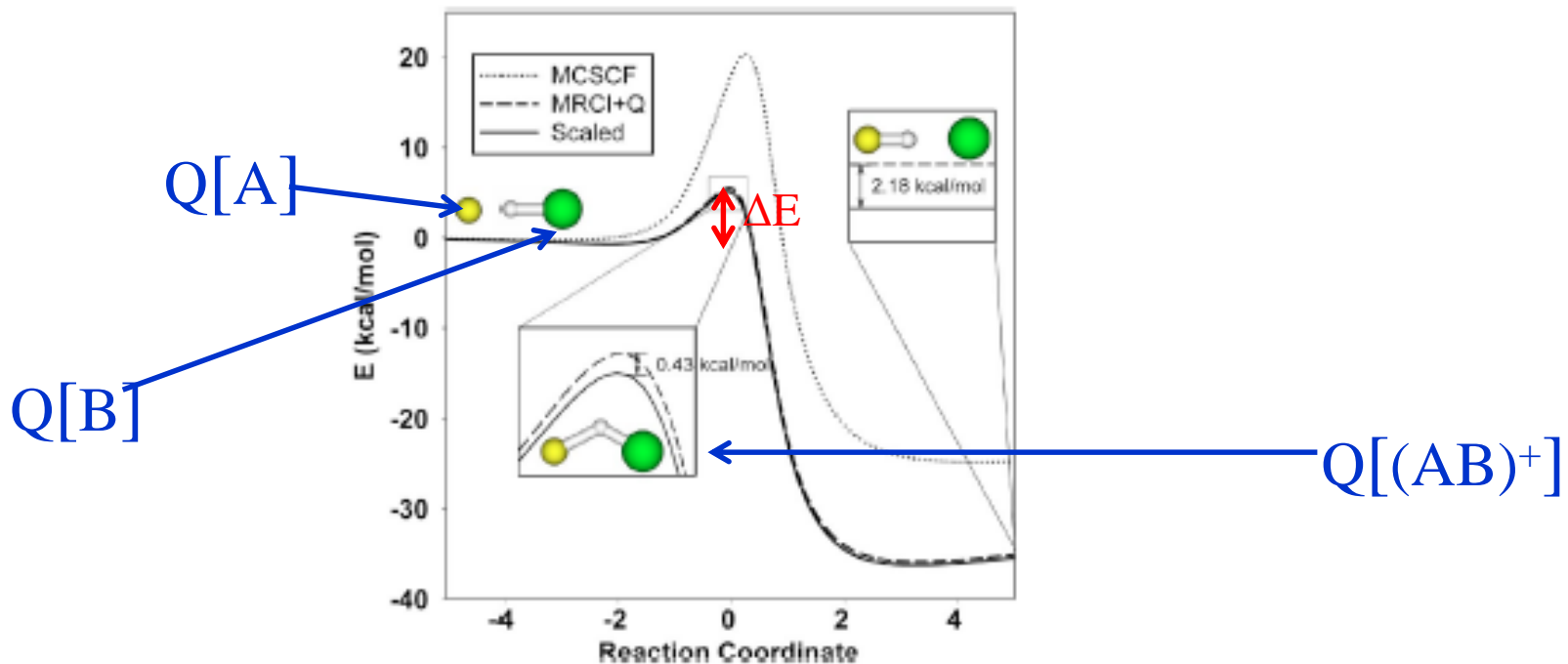
K^{\ddagger} is the thermal rate constant that depends on temperature

Things Needed To Calculate Rate Constant

$$K^+ = \frac{Q[(AB)^+]}{Q[A]Q[B]} \exp\left[-\frac{\Delta E}{k_B T}\right]$$

Q is the partition function of the respective molecules

DE is the energy difference from the reactant to the barrier



Partition Function 1

$$Q_{trans} = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} V = \left(\frac{2\pi m k_B T}{h^2} \right)^{3/2} \frac{k_B T}{P}$$

Usually you consider 1atm pressure

$$\begin{aligned} Q_{electronic} &= D_0 \exp[-\varepsilon_0 / k_B T] + D_1 \exp[-\varepsilon_1 / k_B T] \\ &\quad + D_2 \exp[-\varepsilon_2 / k_B T] + \dots \\ &= D_0 \end{aligned}$$

D is the degeneracy of the electronic state, usually only consider ground electronic state

Partition Function 2

$$Q_{rot} = \frac{\pi^{1/2}}{\sigma_r} \left(\frac{T^{3/2}}{(\theta_A \theta_B \theta_C)^{1/2}} \right) \quad \theta_{A,B,C} = \frac{h^2}{8\pi^2 I_{A,B,C} k_B}$$

I is the moment of inertia around the respective axis

$$Q_{vib} = \prod_i^{N_{vib}} \frac{1}{1 - \exp\left[-\frac{h\nu_i}{k_B T}\right]}$$

ν_i is the vibrational frequency of the i -th vibrational mode

Normal Mode Vibration

First we consider mass-weight Cartesian Coordinates

$$q_1 = m_1^{1/2} \Delta X_1; q_2 = m_1^{1/2} \Delta Y_1; q_3 = m_1^{1/2} \Delta Z_1; q_4 = m_2^{1/2} \Delta x_2; \dots q_{3N} = m_N^{1/2} \Delta Z_N$$

Next expand the potential energy to second term near equilibrium

$$V = V(0) + \sum_I^{3N} K_I q_I + \frac{1}{2} \sum_I^{3N} \sum_J^{3N} K_{IJ} q_I q_J = \frac{1}{2} \sum_I^{3N} \sum_J^{3N} K_{IJ} q_I q_J$$

Total energy is given as $E = \frac{1}{2} \sum_I^{3N} \dot{q}_I^2 + \frac{1}{2} \sum_I^{3N} \sum_J^{3N} K_{IJ} q_I q_J$

Cross term

If we diagonalize K_{IJ} $E = \frac{1}{2} \sum_I^{3N-5/6} \dot{Q}_I^2 + \frac{1}{2} \sum_I^{3N-5/6} \lambda_I Q_I^2$

Motion described by $3N-6$ (5 for linear molecule) **NORMAL MODES**

$$Q_I = \sum_{J=1}^{3N} L_{IJ} q_J \quad I = 1, 3N - 5/6$$

5/6 Modes that are ignored have zero λ_I **TRANSLATION/ROTATION**