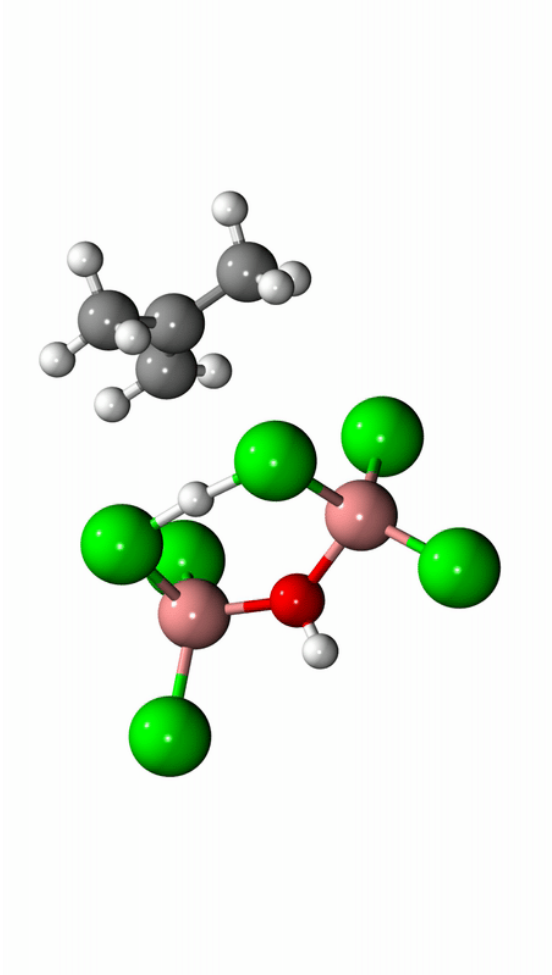
After Mid-Semester – Molecular level understanding of chemical processes – interaction of atoms: the bond breaking and forming will be explored through the trailblazing rate theories of Bell- Evans-Polanyi and the Nobel winning electronic structure models of Fukui-Hoffmann, Ertl, and Kohn-Pople.

Quiz-2: Oct 25th, 2024 (Fri)

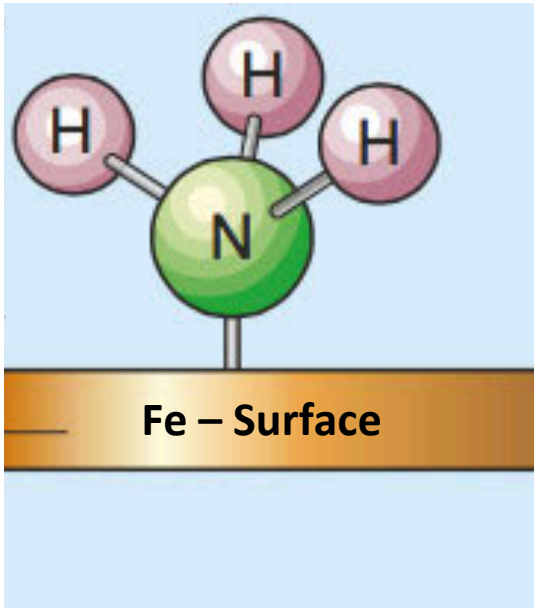
End-Semester Examinations: Nov 17–26, 2024

“molecular level understanding to chemical processes”



Chemical processes

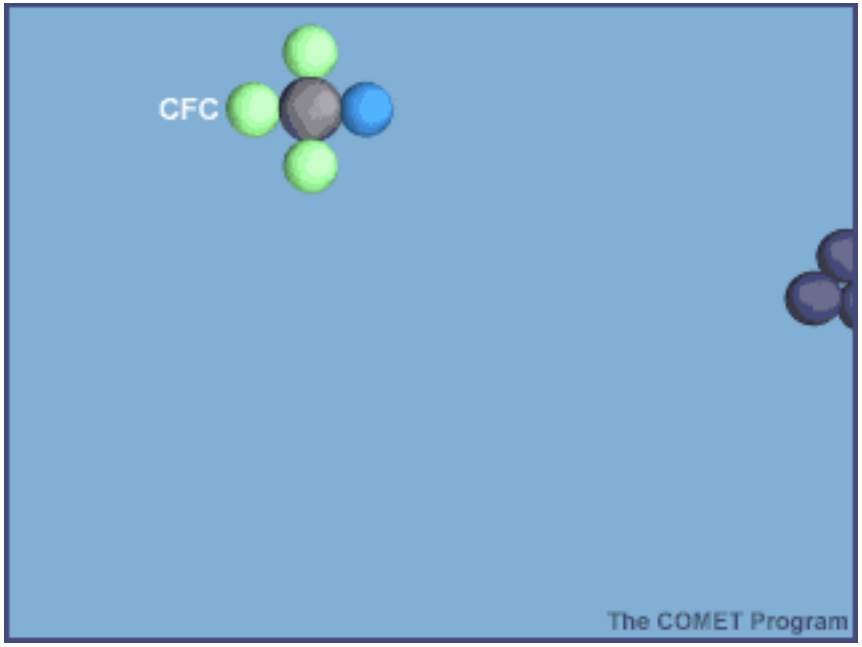
…….



Ertl

“molecular level understanding to chemical processes”

Gas phase reactions….

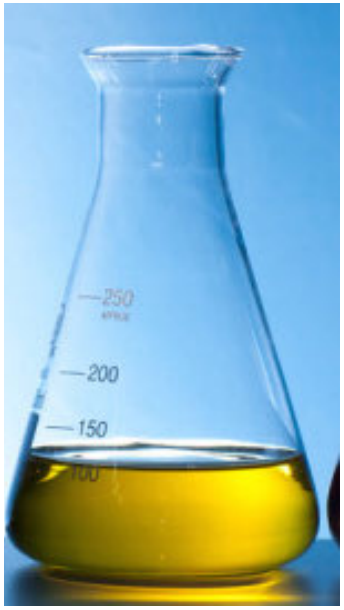


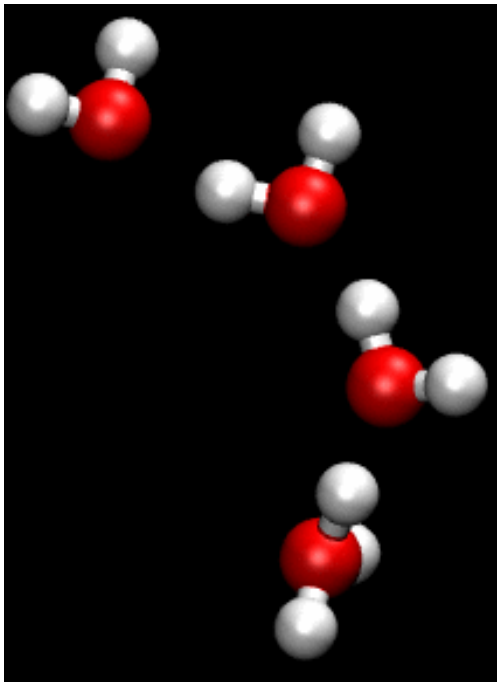
“molecular level understanding to chemical processes”

Solution phase reaction….

“molecular level understanding to chemical processes”

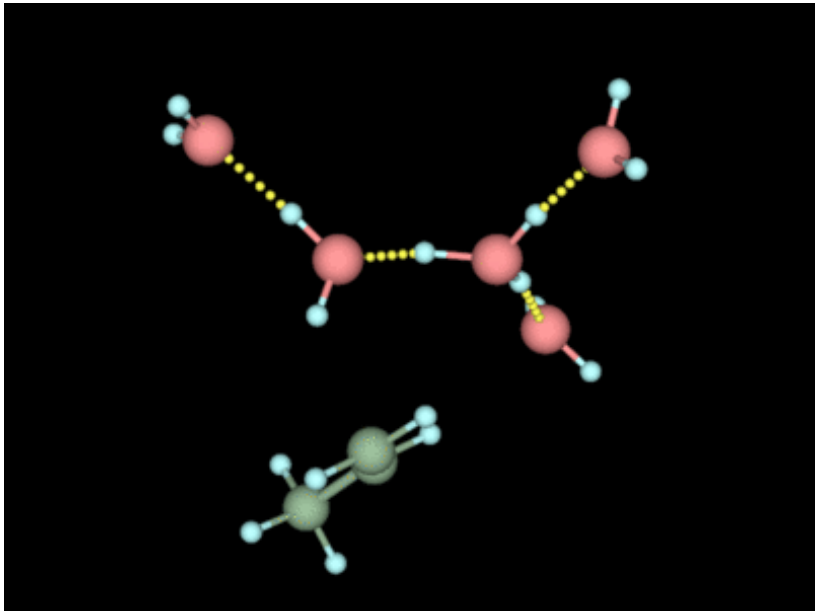
Solution phase reactions….





“molecular level understanding to chemical processes”

Solution phase reactions….

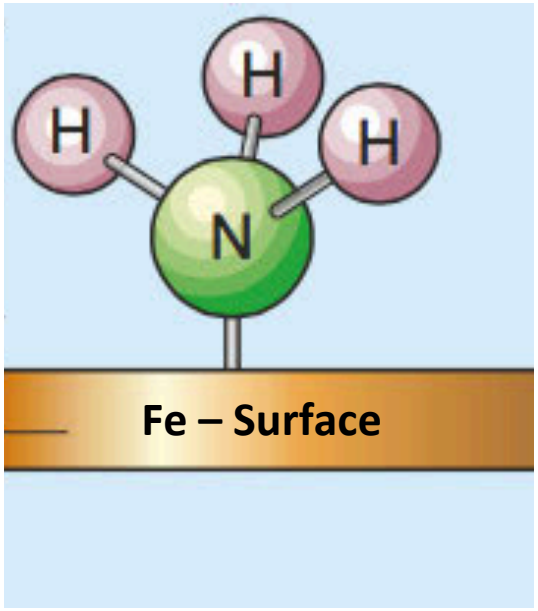


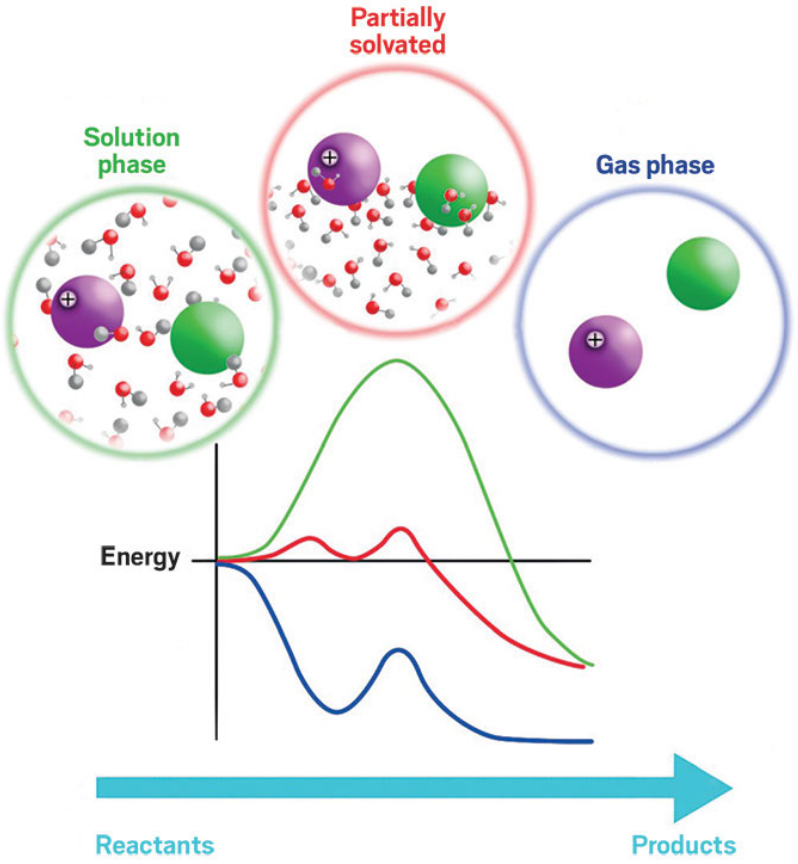
$$\hat{H}\psi(r) = E\psi(r)$$

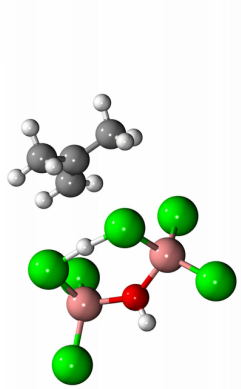
$$k_{\mathrm{TST}} = \frac{k_{\mathrm{B}}T}{h}(c^{\mathrm{o}})^{\Delta\nu^{\dagger}} \exp\left(-\frac{\Delta G^{\mathrm{o}\dagger}}{RT}\right)$$

Chemical processes

.....

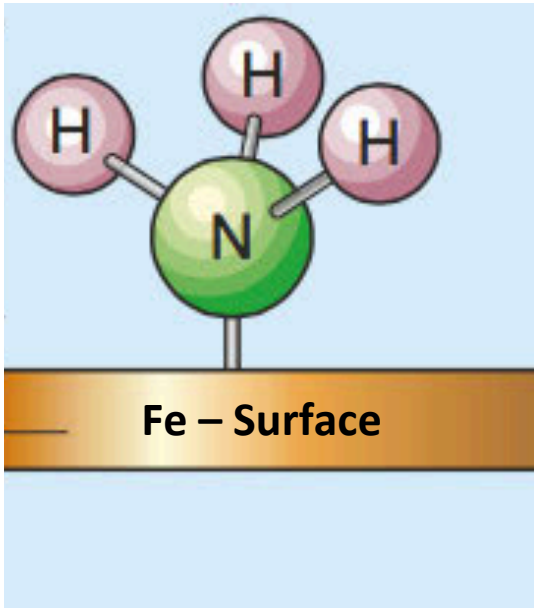




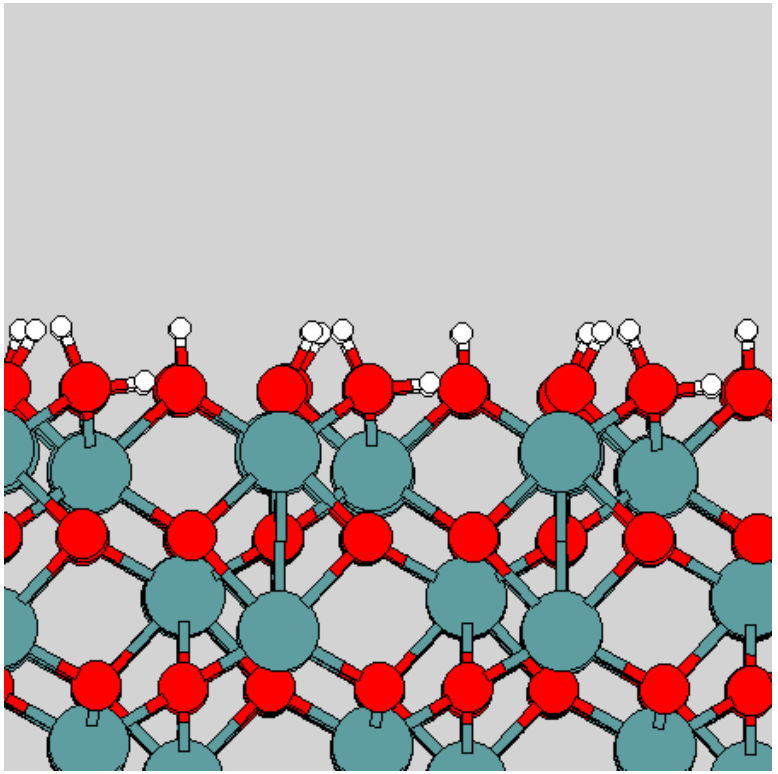


“molecular level understanding to chemical processes”

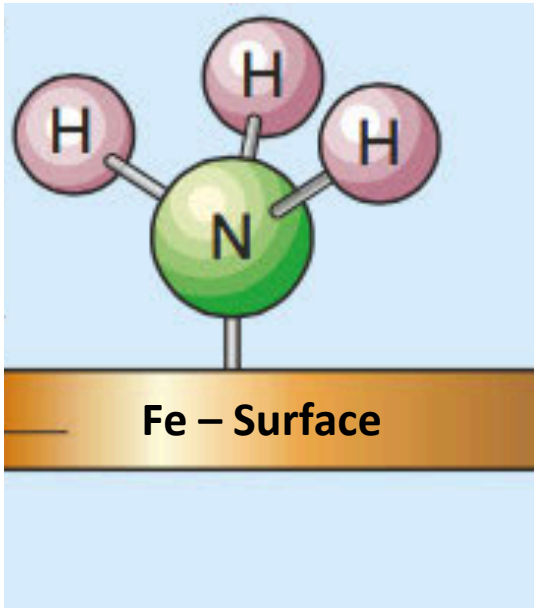
Chemical processes on solid surfaces …….



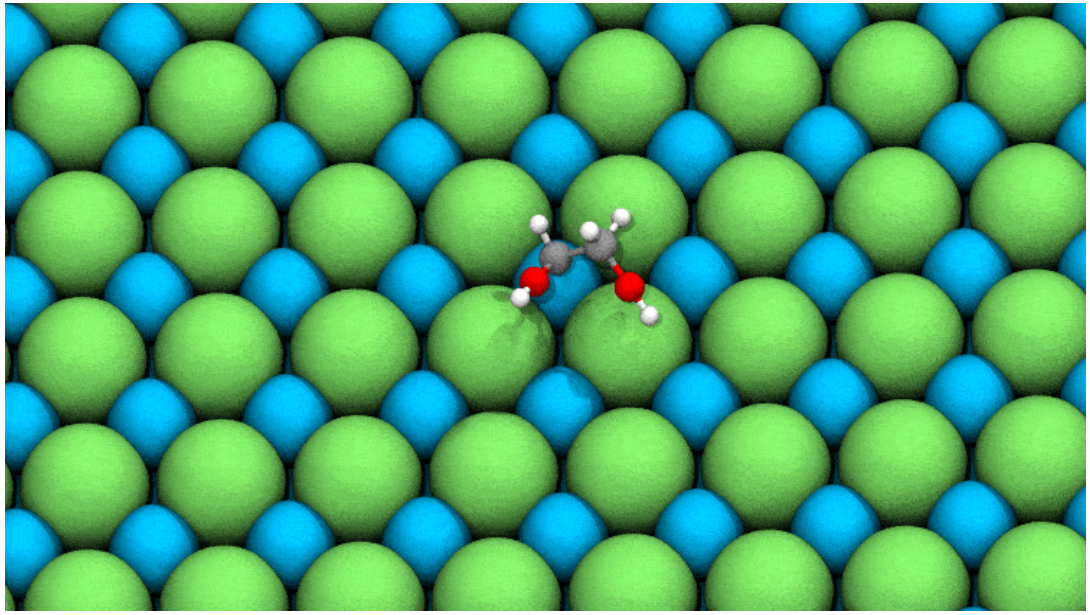
Surface reaction….



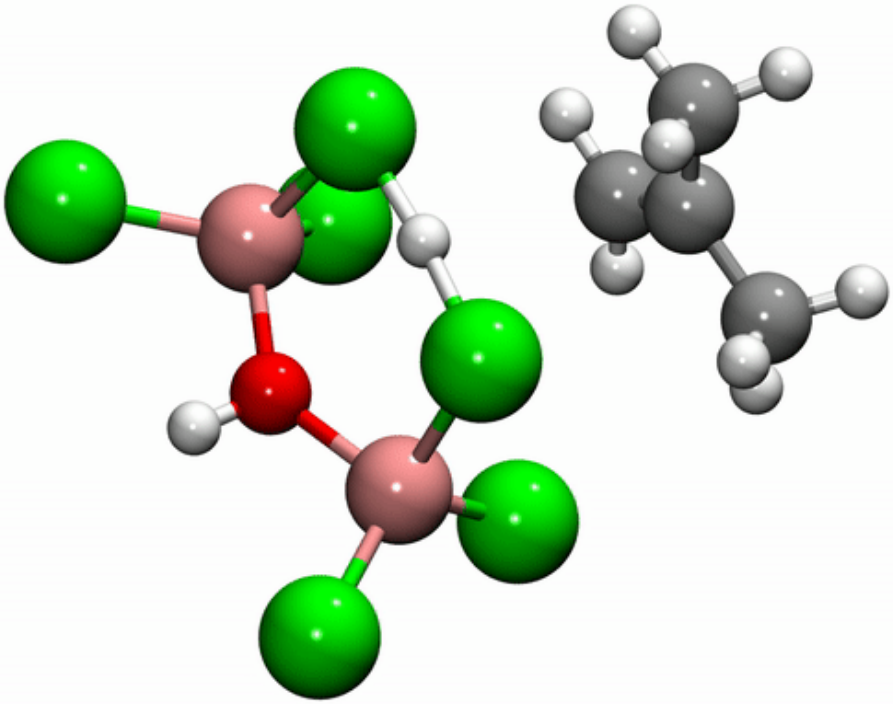
Chemical processes on solid surfaces …….



Surface reaction….

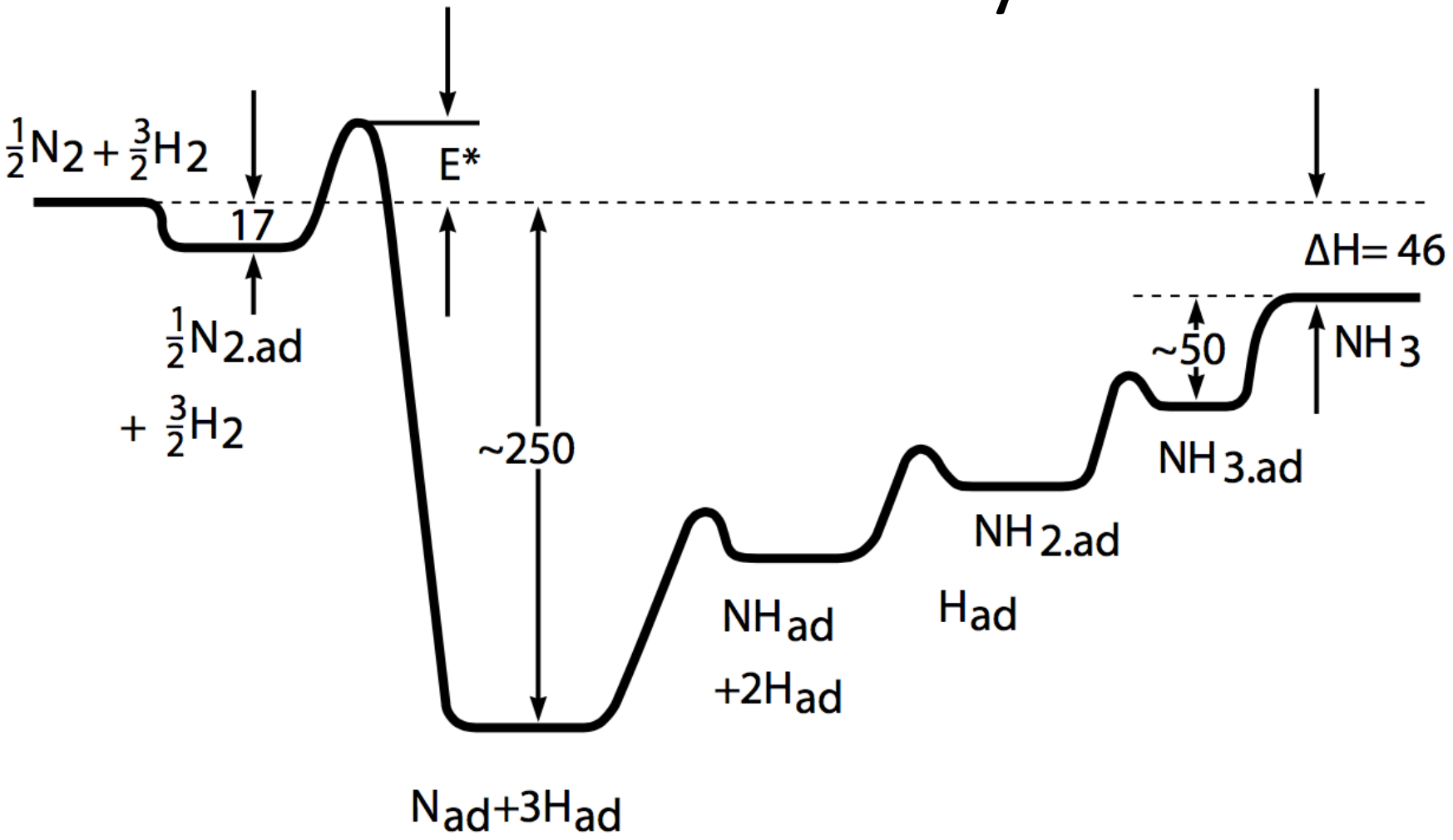


Bond Breaking and Bond Forming



Substrate and Reactant Interaction:
molecular level understanding to chemical processes

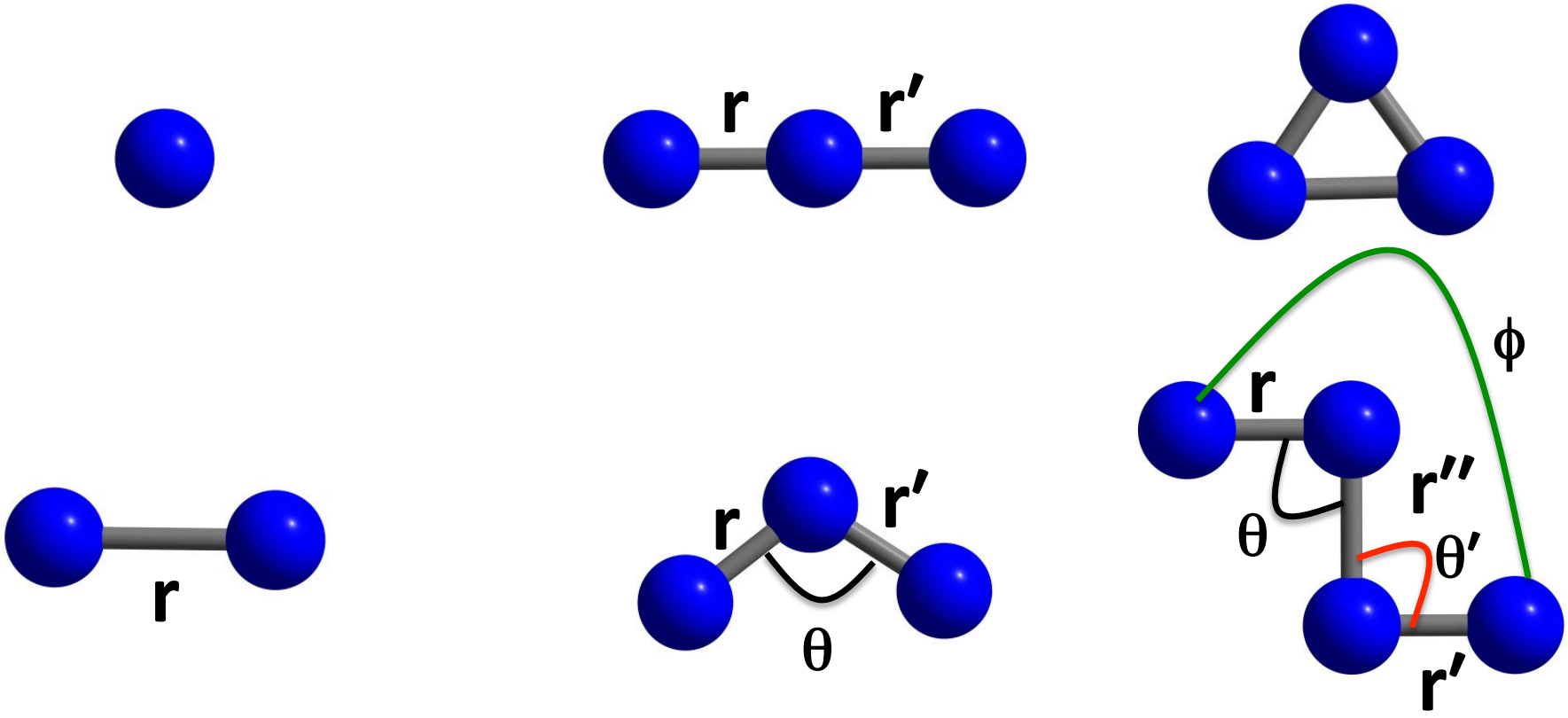
Chemical Reaction Dynamics

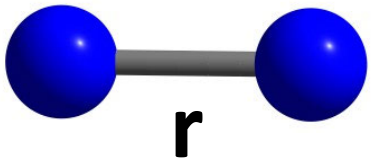


An energy diagram showing the progression of the reaction from the reactants N_2 and H_2 to the product NH_3. Energies are given in units of kJ/mol. (Adapted from Ertl 1983)

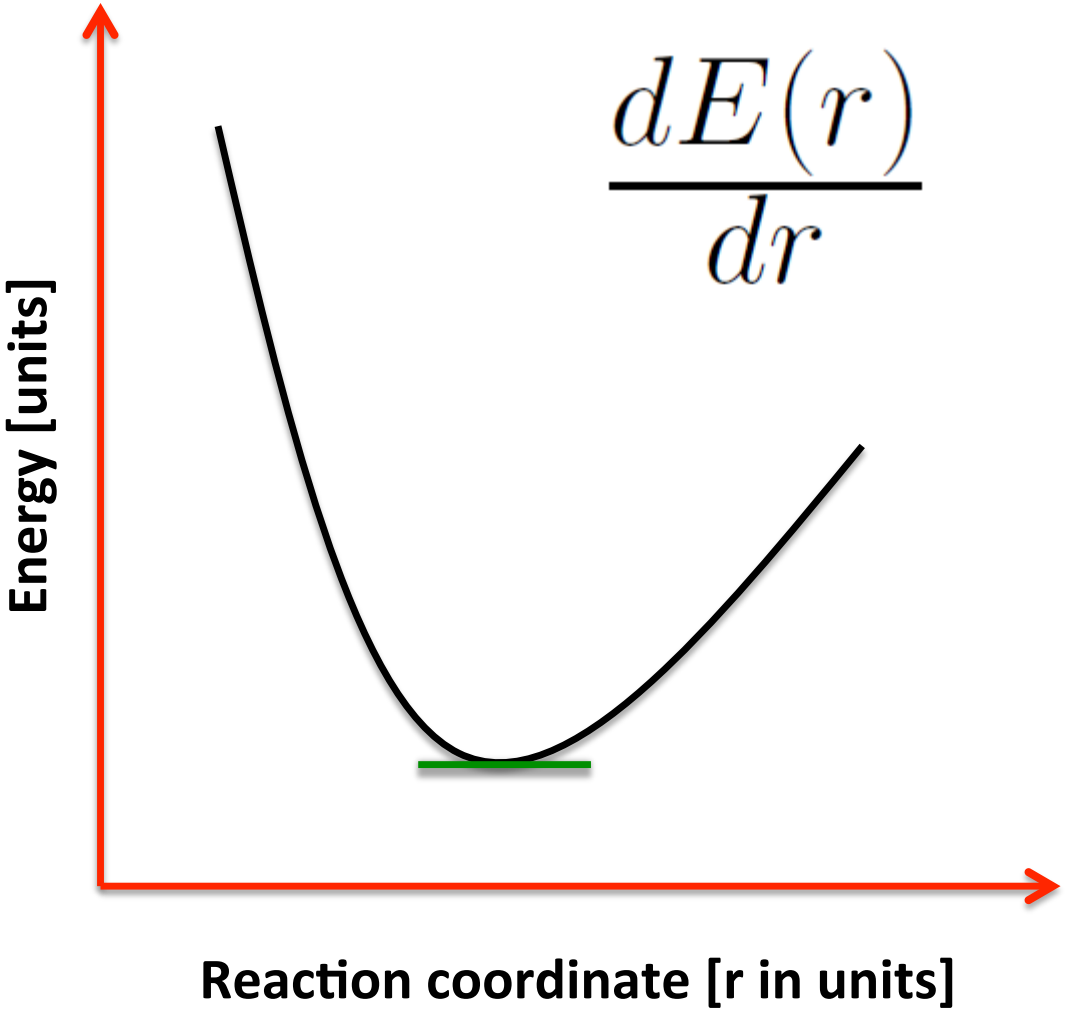
Configurations

For a configuration! Of course!

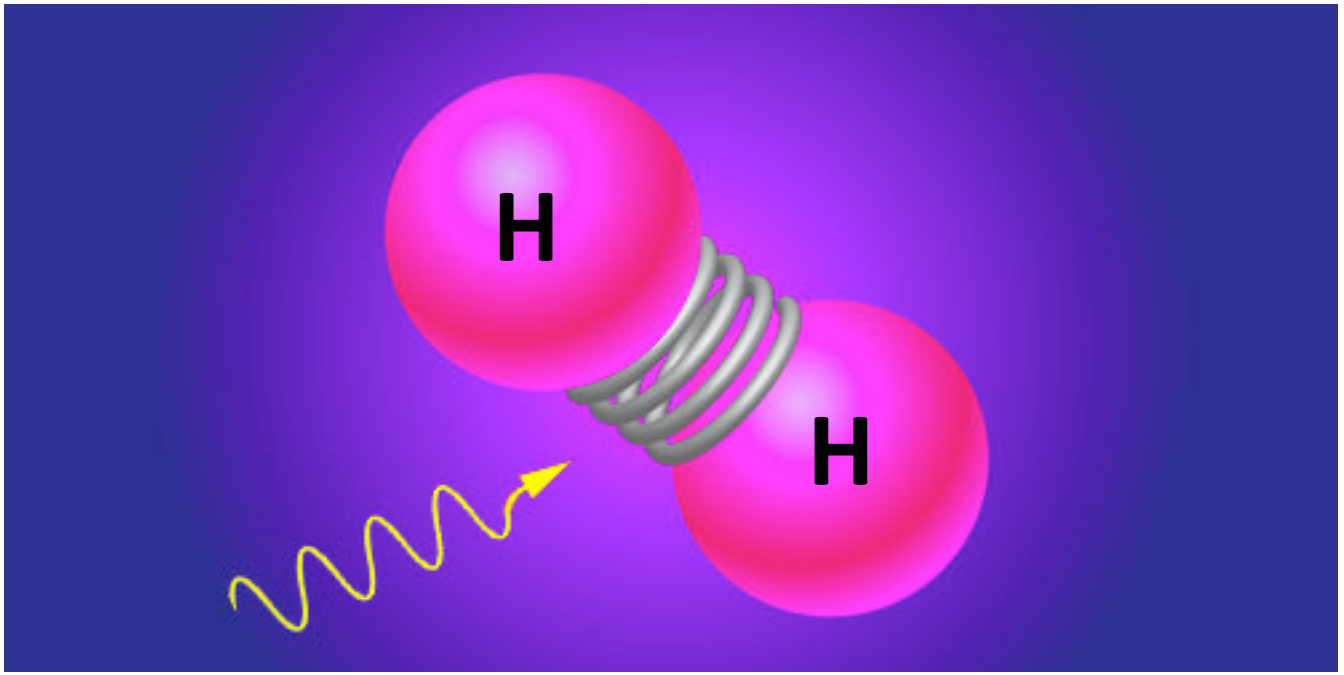


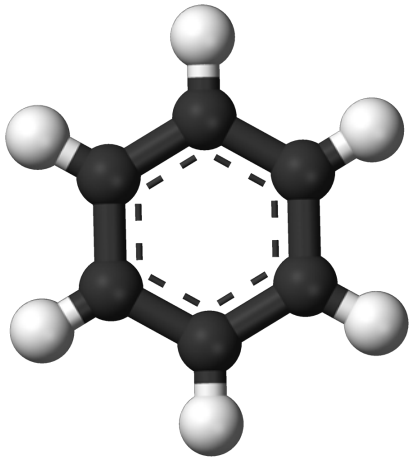


Interacting system



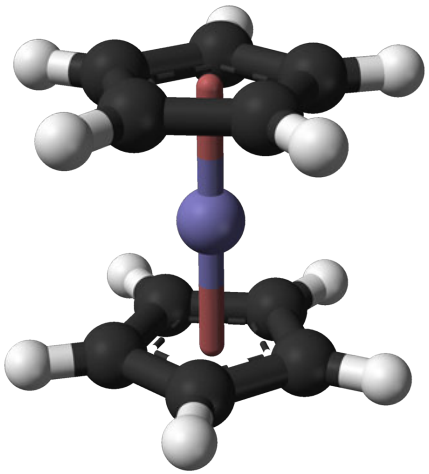
H_2 molecule



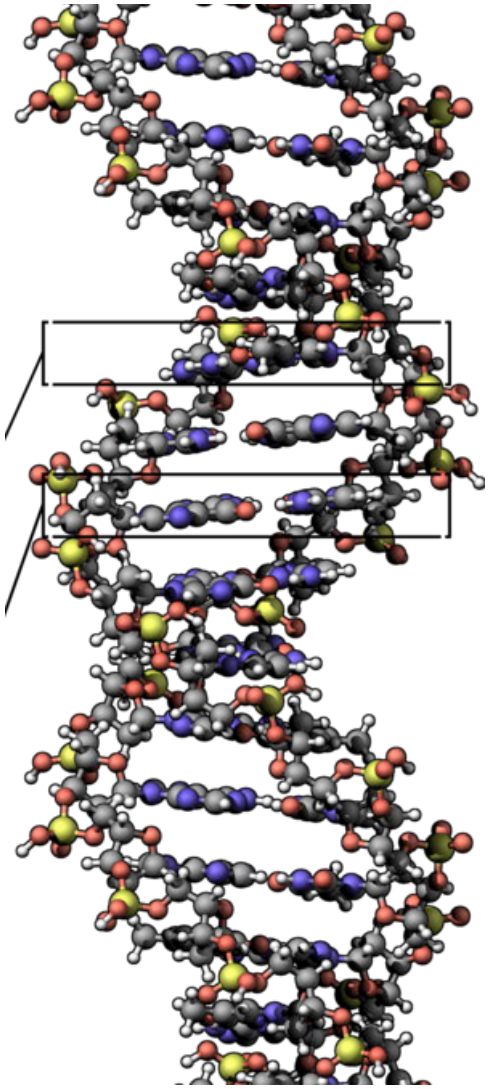


An ubiquitous molecule in chemistry and biology

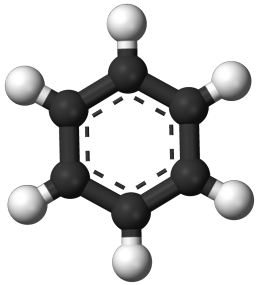
One of the most frequent motifs found in drug molecules

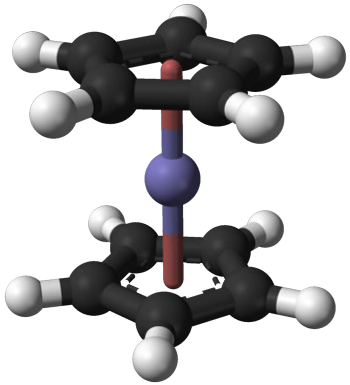


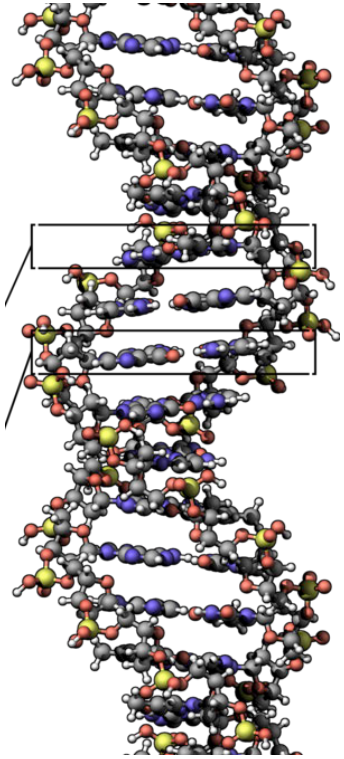
Although ferrocene is not the first organometallic compound, but its discovery began M-C bond chemistry (***organometallic***) as a separate area of chemistry.

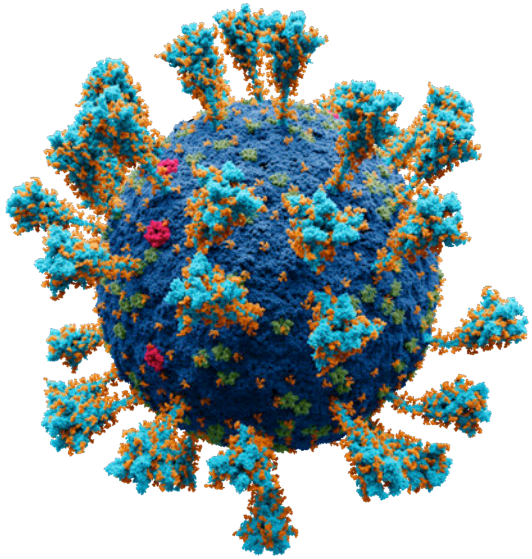


The molecules of Life









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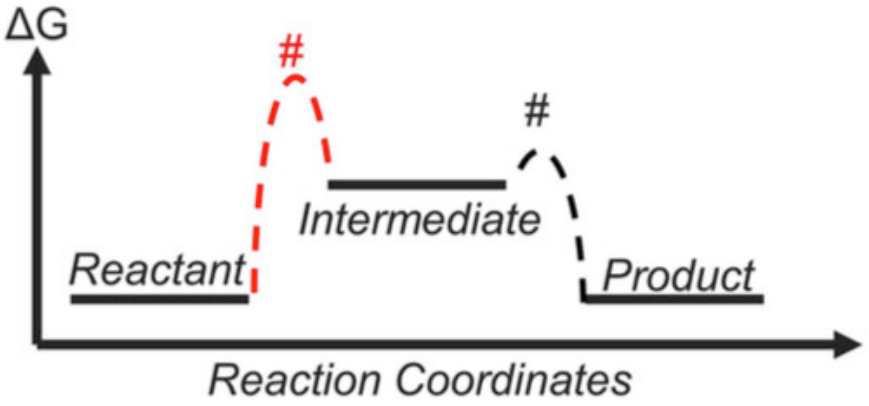
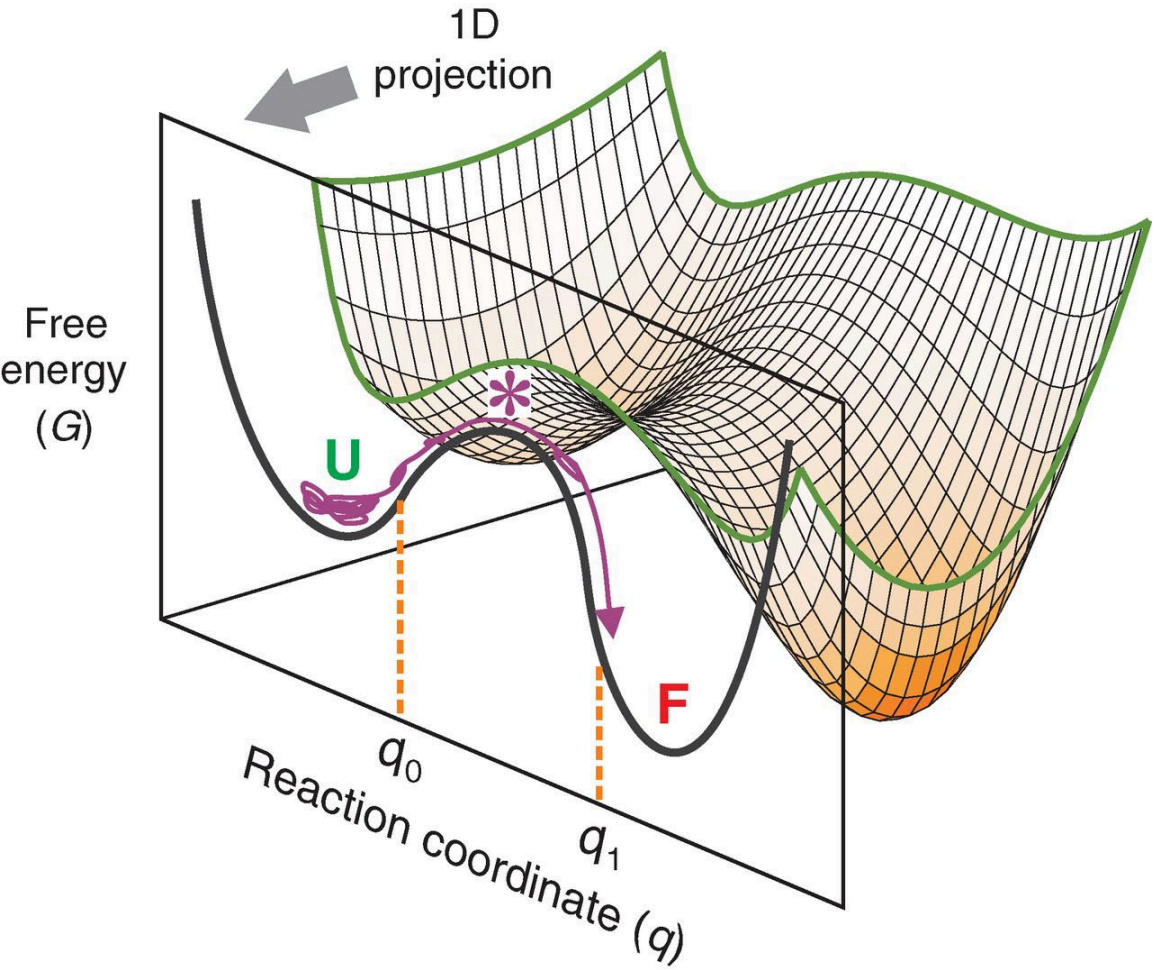
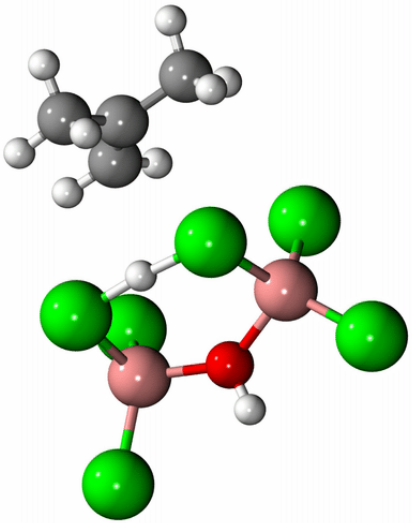






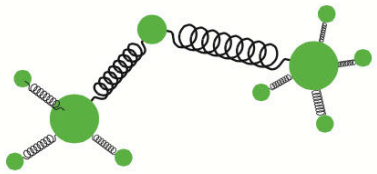
The Big Picture

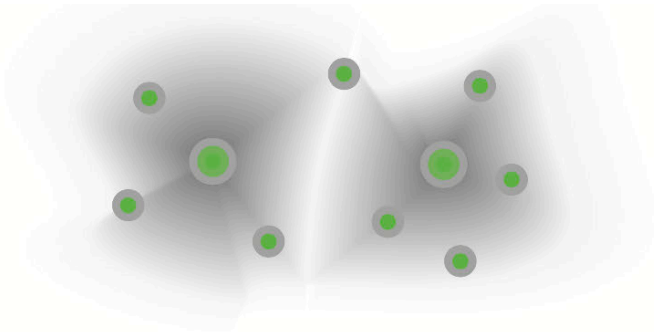
molecular level understanding of chemical processes

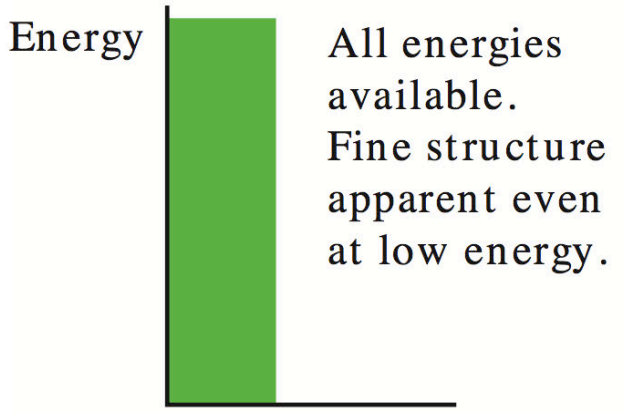
Quantum Mechanics

Quantum Theory?

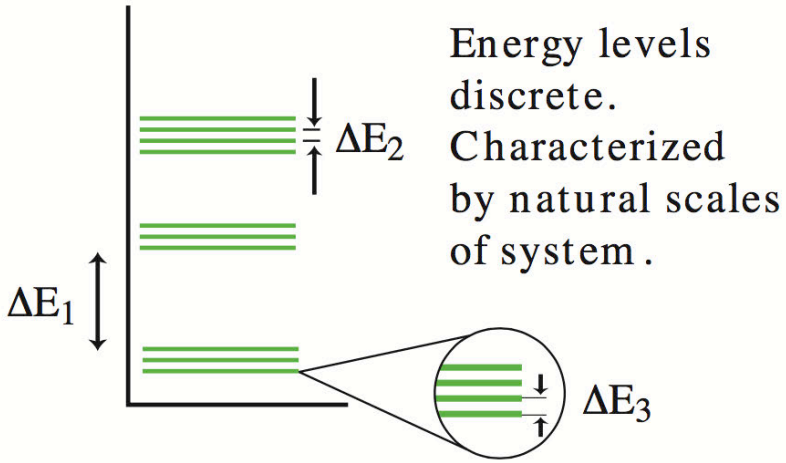
It is a theory in which energy exists only in discrete quantities, called quanta







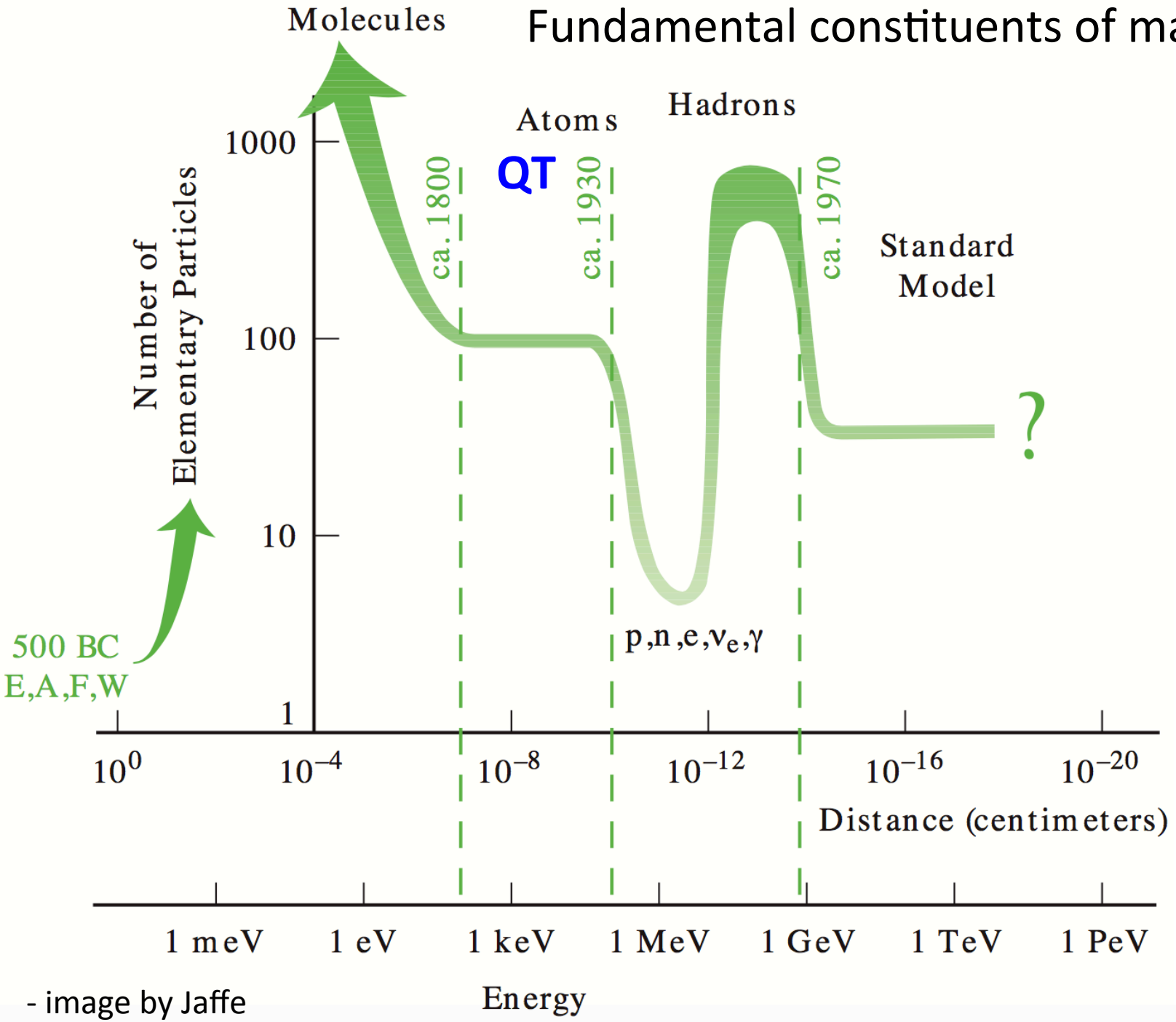
Energy Levels of a Classical System



Energy Levels of a Quantum System

- image by Jaffe

Fundamental constituents of matter



- image by Jaffe

Quantum Mechanics?

Quantum theory led to the development of mathematical formalisms based on matrices and differential equations (**DE**) to understand the interaction between matter and radiation known as quantum mechanics. The **DE** bears the similarities to those in classical theories of waves (wave mechanics)

Schrödinger Wave Equation

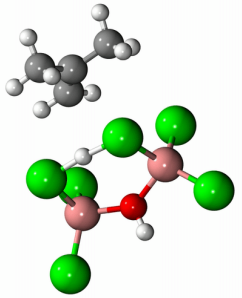
$$\hat{H}\psi(r) = E\psi(r)$$

$$-\frac{\hbar^2}{2m}\frac{d^2\psi(x)}{dx^2} + V(x)\psi(x) = E\psi(x)$$

“Nature isn't classical, dammit, and if you want to make a simulation of nature, you'd better make it quantum mechanical, and by golly it's a wonderful problem, because it doesn't look so easy”

The big picture

Schrödinger equation:



$$\hat{H}\psi(r) = E\psi(r)$$

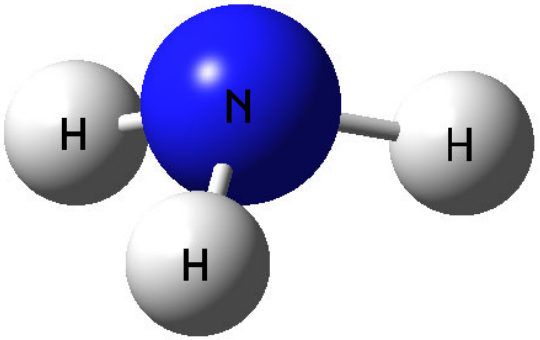
$$\hat{H} = -\frac{1}{2}\sum_{\alpha}\nabla_{\alpha}^{2} - \frac{1}{2}\sum_{i}\nabla_{i}^{2} + \frac{1}{2}\sum_{\alpha\neq\beta}\frac{Z_{\alpha}Z_{\beta}e^{2}}{R_{\alpha}-R_{\beta}} -$$

$$\frac{1}{2}\sum_{\alpha,i}\frac{Z_{\alpha}e^{2}}{r_{i}-R_{\alpha}} + \frac{1}{2}\sum_{i\neq j}\frac{e^{2}}{r_{i}-r_{j}}$$

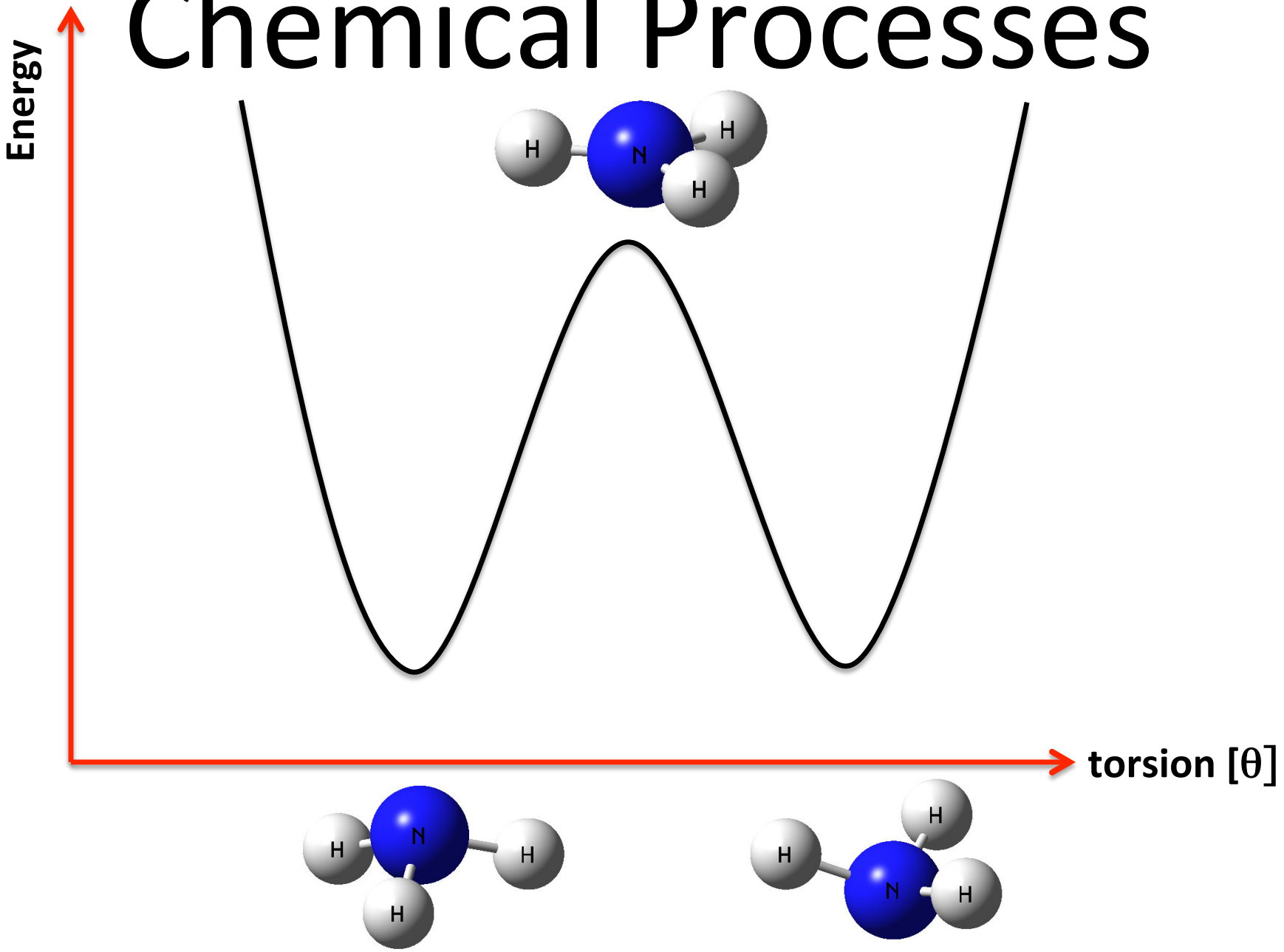
Note: The Hamiltonian does not include the external electric and magnetic interactions.

“Schrodinger's equation cannot be solved exactly for atoms with more than one-electron”

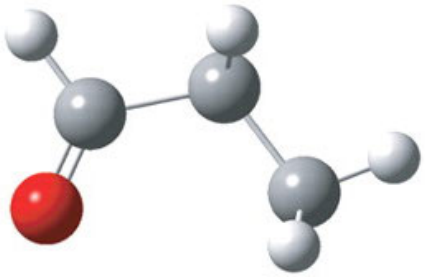
Chemical Processes



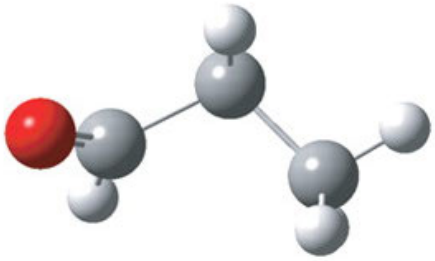
Chemical Processes



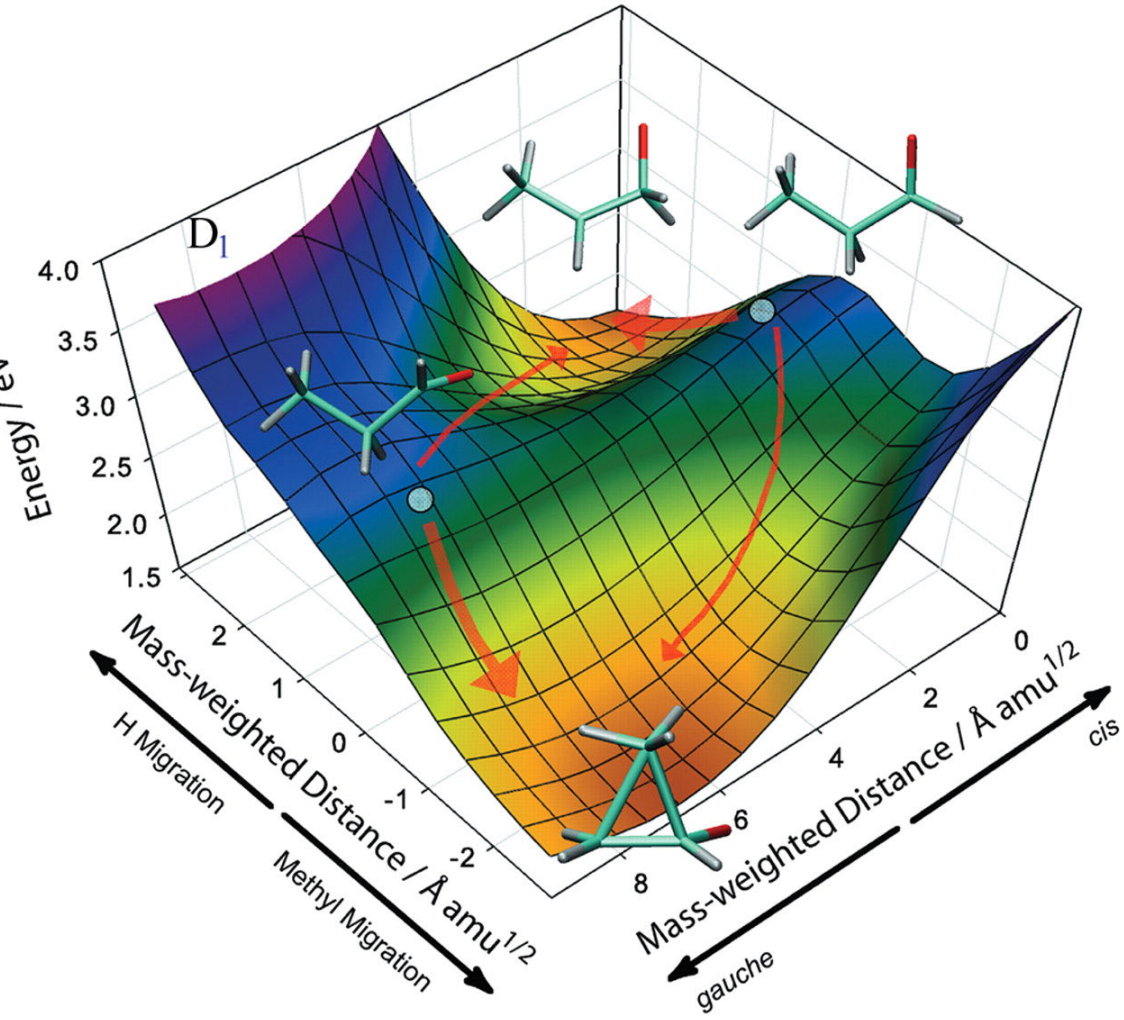
Conformationally Controlled Chemistry



cis-$CH_3CH_2CHO^+$

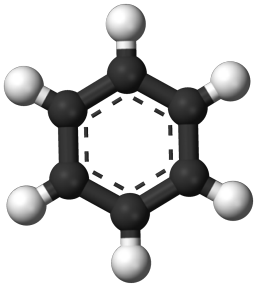


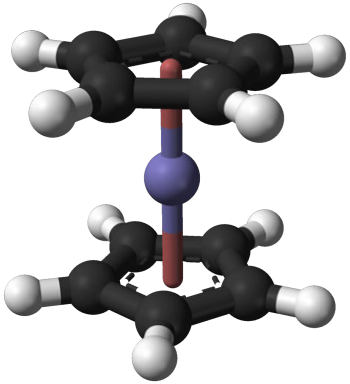
gauche-$CH_3CH_2CHO^+$

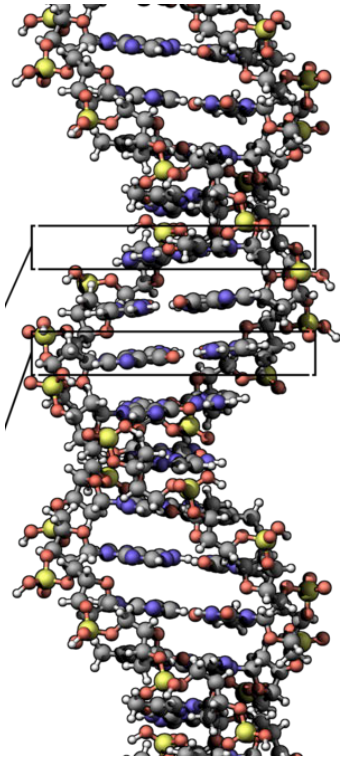


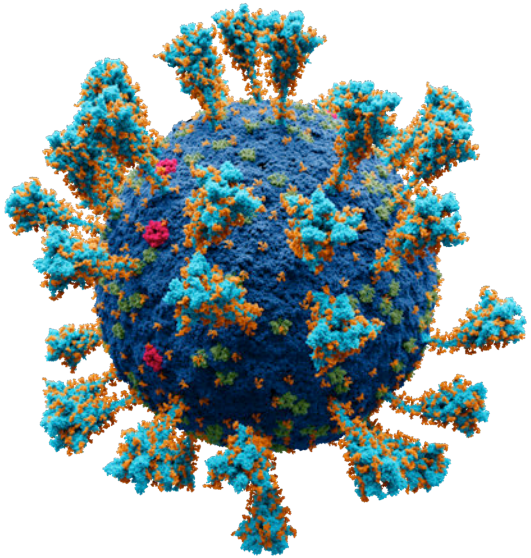
Science, 315, 1561 (2007)

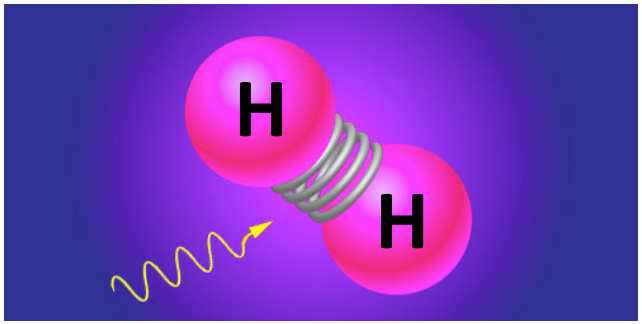

H
H

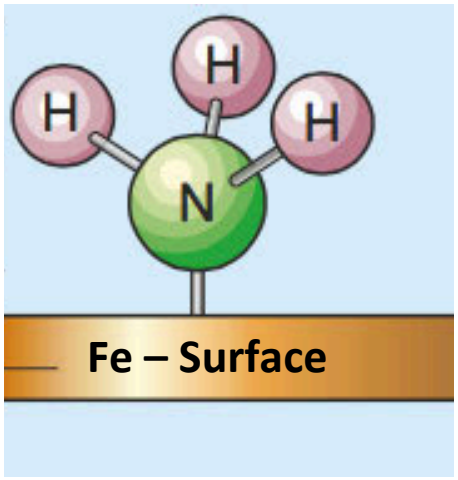


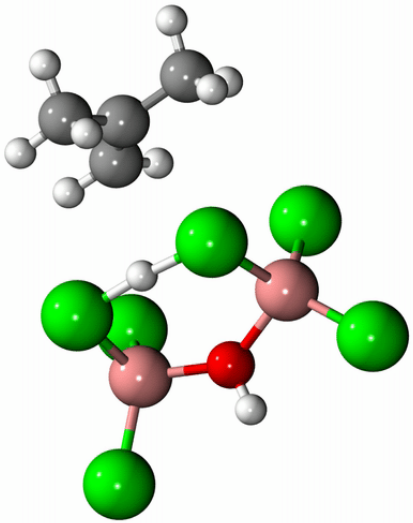


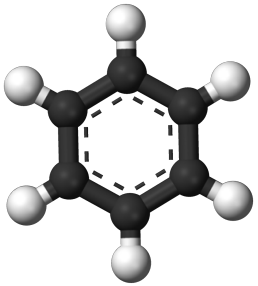


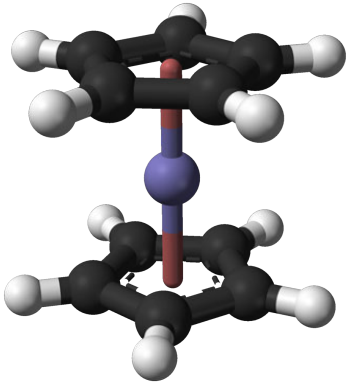


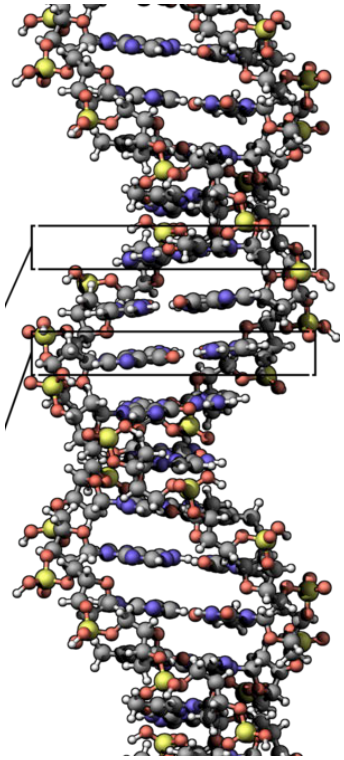

H
H

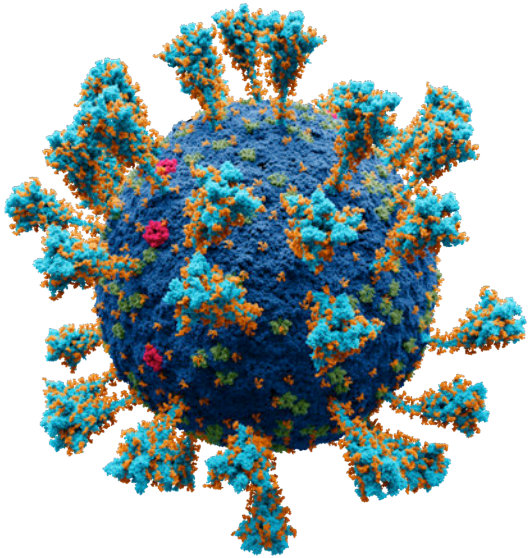

H
H
H
N
Fe – Surface









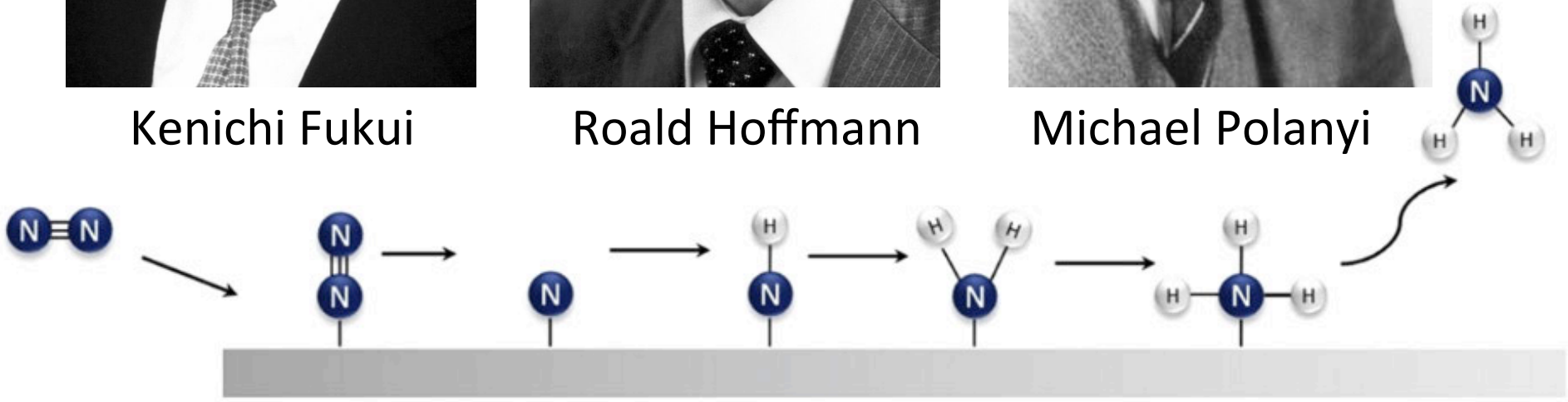


Molecular level understanding of chemical processes

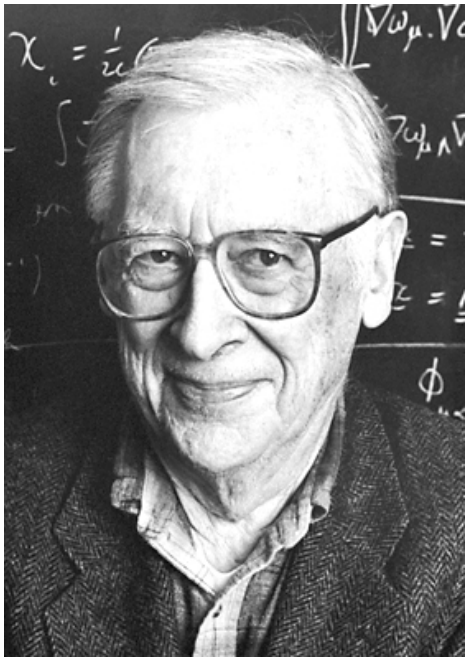
Kenichi Fukui

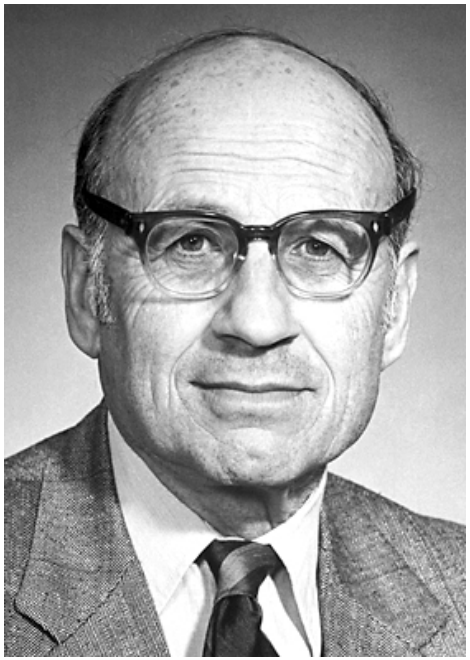
Roald Hoffmann

Michael Polanyi

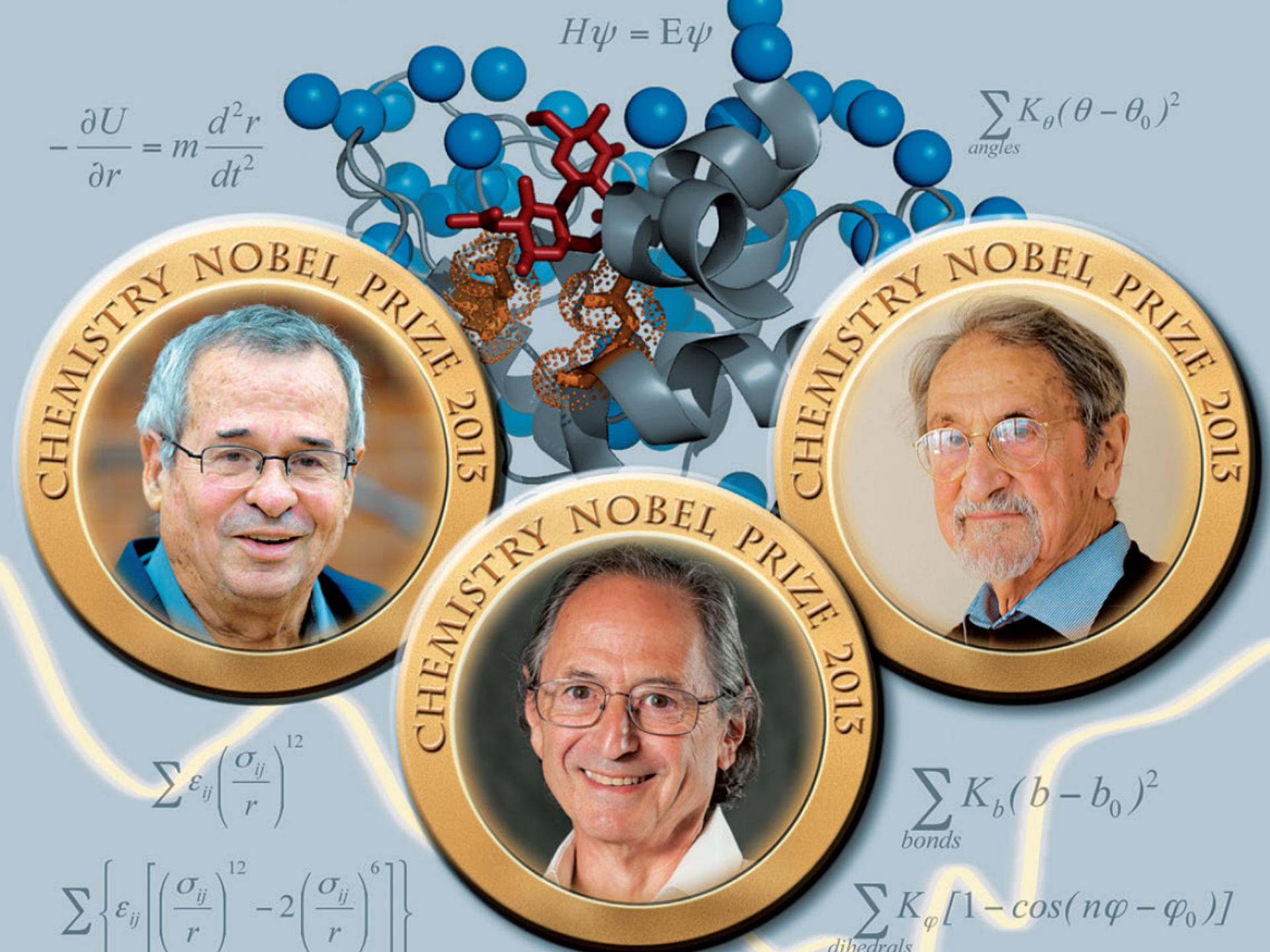


The Nobel Prize in Chemistry 1998





The Nobel Prize in Chemistry 1998 was awarded to John A. Pople (*left*) "for his development of computational methods in quantum chemistry" and Walter Kohn (*right*) "for his development of the density-functional theory (DFT)" .


$H\psi = E\psi$
$-\frac{\partial U}{\partial r} = m\frac{d^2r}{dt^2}$
$\sum_{angles} K_\theta(\theta - \theta_0)^2$
CHEMISTRY NOBEL PRIZE 2013
CHEMISTRY NOBEL PRIZE 2013
CHEMISTRY NOBEL PRIZE 2013
$\sum \varepsilon_{ij}\left(\frac{\sigma_{ij}}{r}\right)^{12}$
$\sum_{bonds} K_b(b - b_0)^2$
$\sum\left\{\varepsilon_{ij}\left[\left(\frac{\sigma_{ij}}{r}\right)^{12} - 2\left(\frac{\sigma_{ij}}{r}\right)^{6}\right]\right\}$
$\sum_{dihedrals} K_\varphi[1 - cos(n\varphi - \varphi_0)]$

Chemical Processes

For example, course of chemical reactions – structure and reactivity

The dissociation of hydrogen into atoms.

$$H_2 \xrightarrow{>3500\ K} H + H$$

$D(H_2)$ ~ 100 kcal/mol

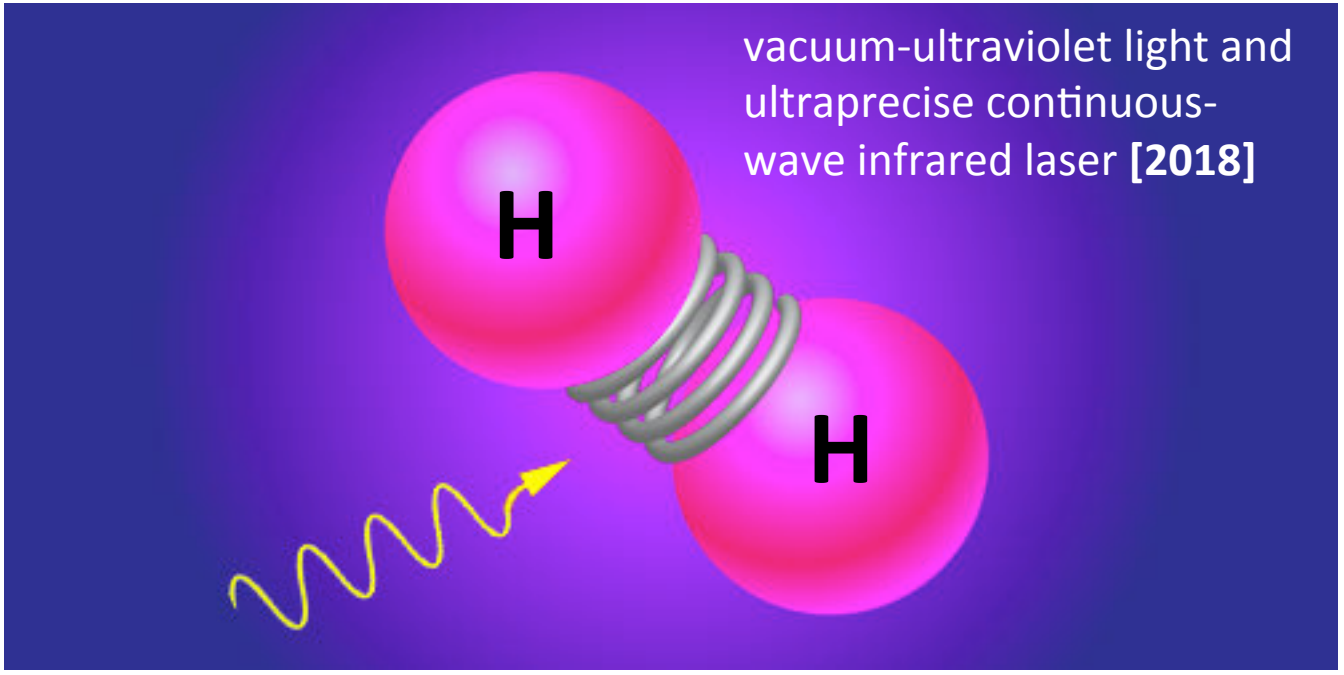
$D(H_2)$ 5.7 eV from Langmuir in 1915
$D(H_2)$ 3.14 eV from H & L in 1927
$D(H_2)$ 4.46 eV from Ubachs et al. in 2018

0.1594	Hartrees
4.336	eV
418.4	kJ/mol
100	kcal/mol
34980	cm^{-1}
4.336	V
50320	K

Chemical Processes

The dissociation of hydrogen into atoms.

$H_2 \longrightarrow H + H \quad D(H_2)\ 4.46\ eV$



Ubachs et al., https://physics.aps.org/synopsis-for/10.1103/PhysRevLett.121.013001 [2018]

before Schrödinger, Werner Heisenberg was awarded the Nobel Prize for developing an alternative (but equivalent) quantum theory, "*whose application led amongst other things to the discovery of the allotropic forms of the hydrogen molecule*". This is based on an early experimental confirmation of the new quantum mechanics: According to this, both protons in the H_2 molecule each possess a nuclear spin which can be aligned either parallel (ortho-H_2) or antiparallel (para-H_2) to each other. The coupling of this angular momentum

– Ertl (Angewandte Chemie, 2015)

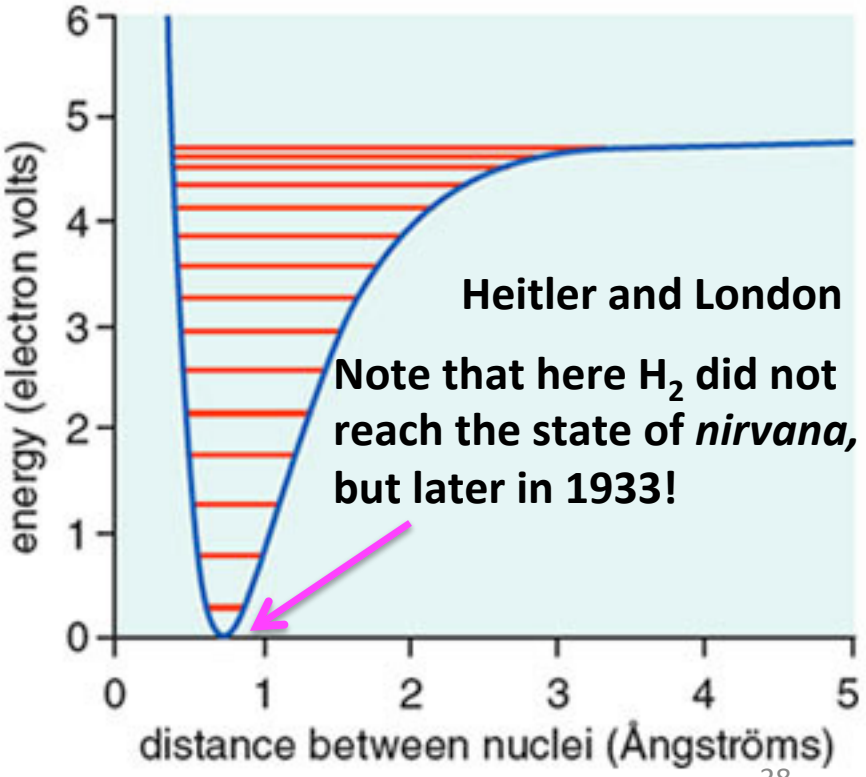
Molecular level understanding of chemical processes

The dissociation of hydrogen into atoms.

$H_2 \longrightarrow H + H$

$D(H_2)$ 3.14 eV from H & L in 1927

For the first time quantum mechanics "explained" the existence of a molecule. Which classical mechanics coupled with electrostatics, try as it might, couldn't.



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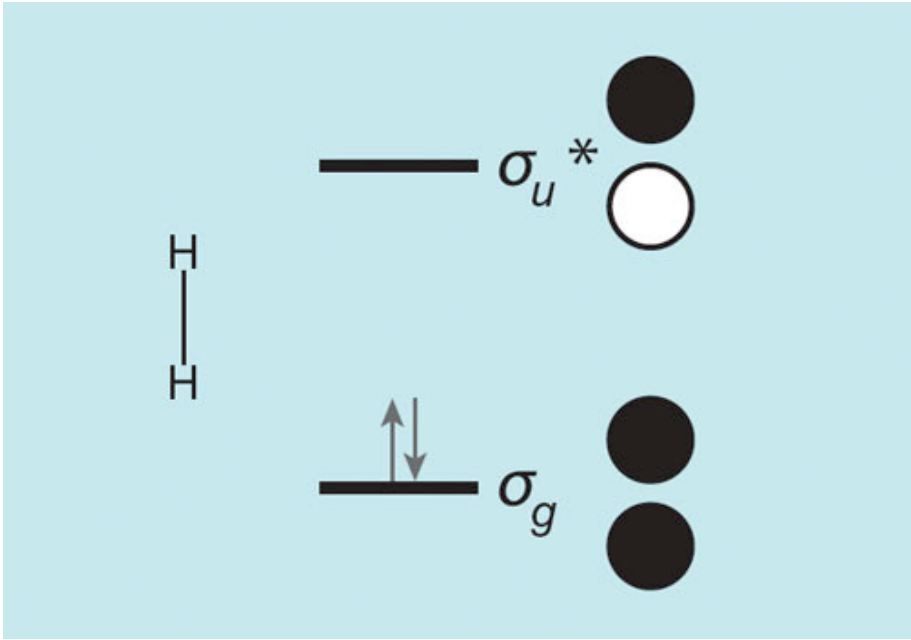
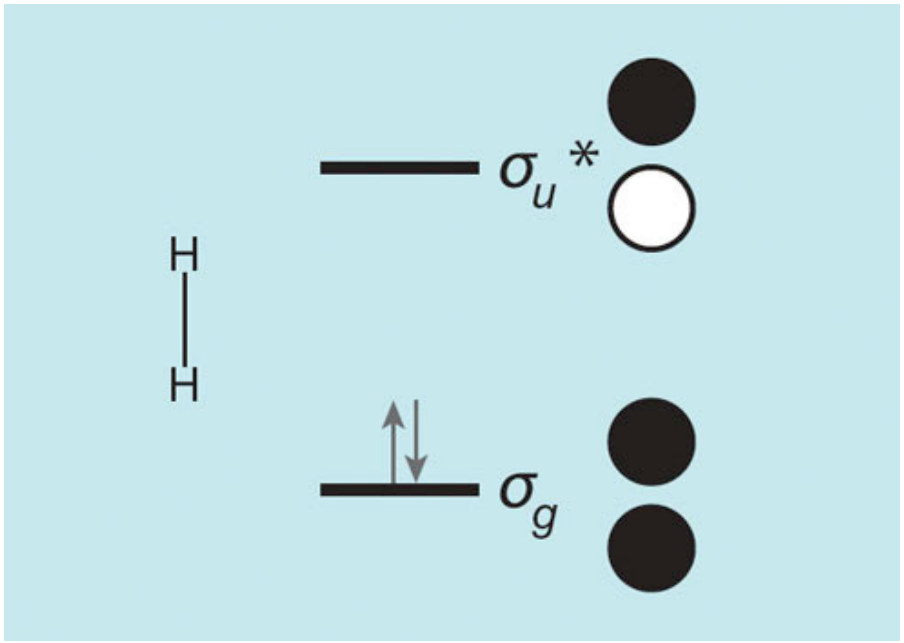


LCAO-MO of H_2

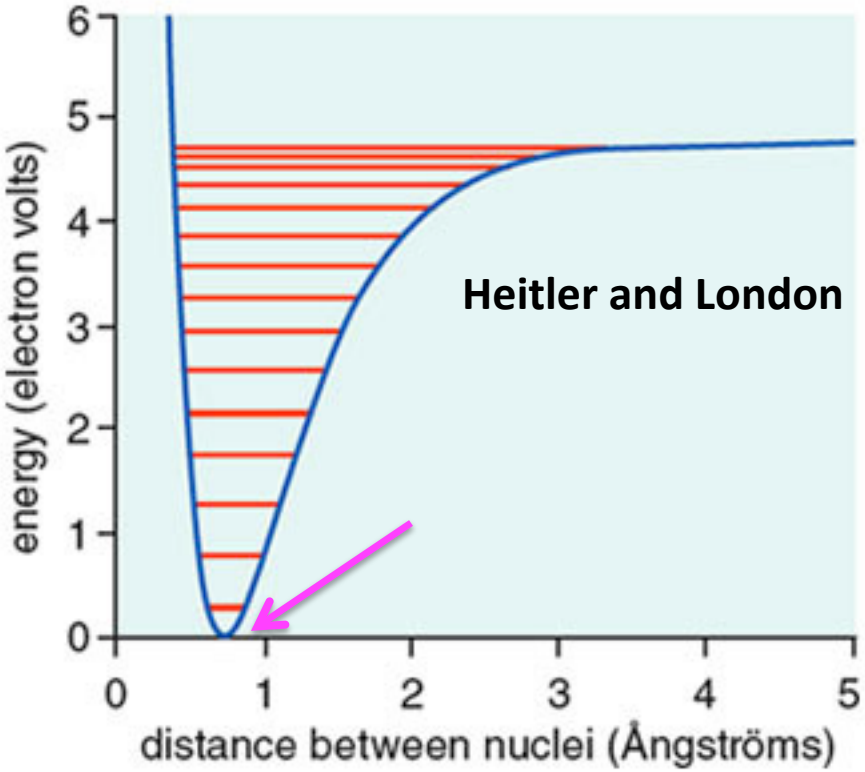
Electronic Structure

The dissociation of hydrogen into atoms.

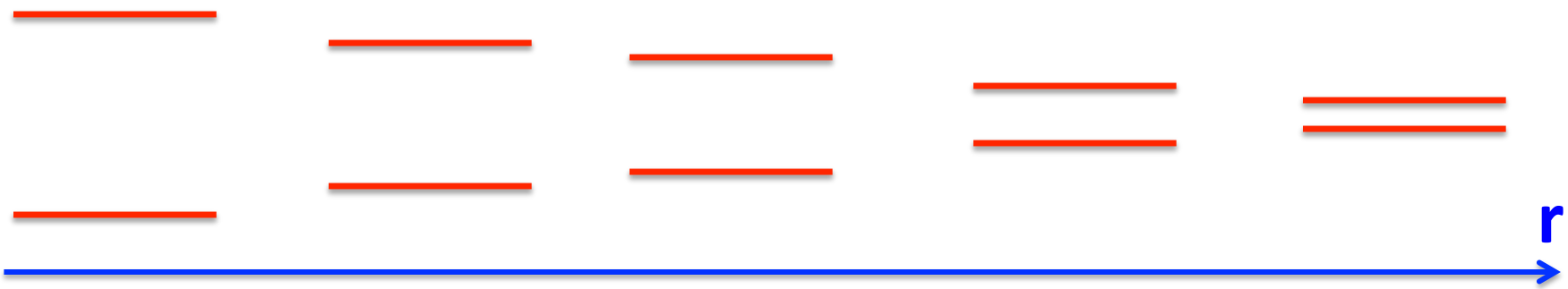
$$H_2 \longrightarrow H + H$$

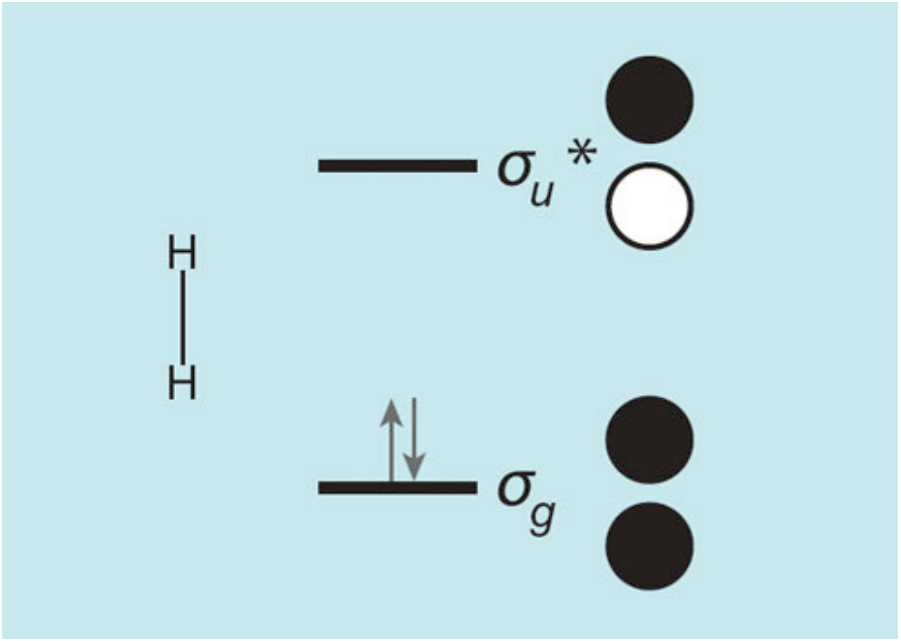


LCAO-MO of H_2



Electronic Structure





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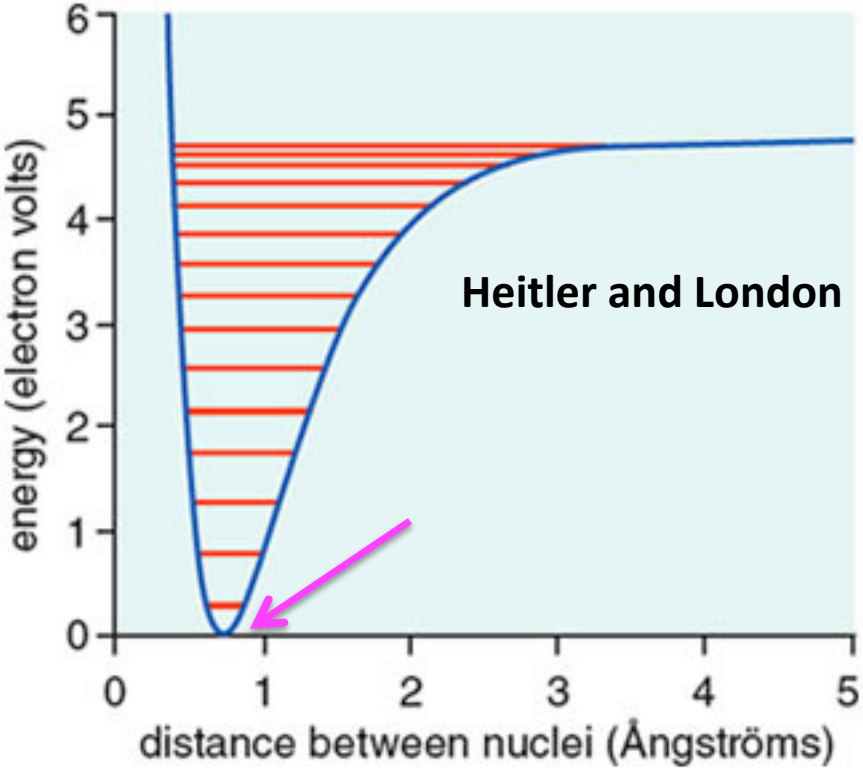


Electronic Structure

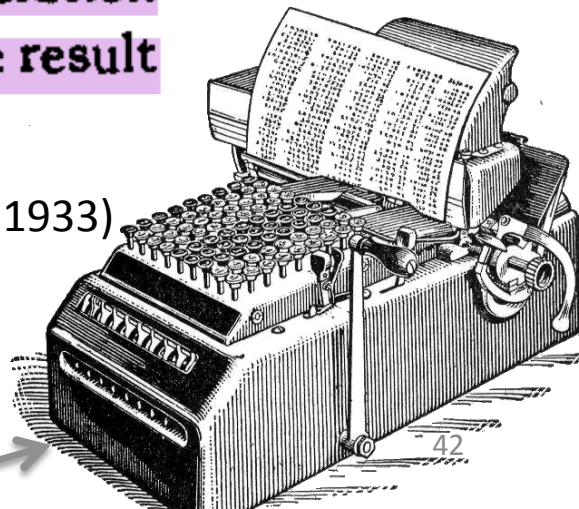
The application of quantum mechanics to chemistry

The dissociation of hydrogen into atoms.

$H_2 \longrightarrow H + H$ $D(H_2)$ 104 kcal/mol or 4.5 eV

energy of H_2 at the potential minimum. Correcting for the zero point vibration we then obtain for the dissociation energy of $H_2D_{H_2} = 4.454 \pm 0.013$ e.v., as the probable result of a complete theoretical treatment of the problem.

– James and Coolidge (1933)



Hand-cranked mechanical calculator (1914)

Things began to move at the beginning of the 1960s when computers came into use for solving these equations…..

Students working on the IBM 1620 computer at Kanpur, circa 1964 (Source: IIT, Kanpur, 1965 Convocation publication, p.23).

Quantum Mechanics of Many-Electron Systems.

By P. A. M. Dirac, St. John's College, Cambridge.

(Communicated by R. H. Fowler, F.R.S.—Received March 12, 1929.)

The underlying laws necessary for the mathematical theory of large parts of physics and the whole of chemistry are thus completely known, and the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.

Proc. R. Soc. Lond. A 1929 123 714-733