Quantum Mechanics of Many-Electron Systems.

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

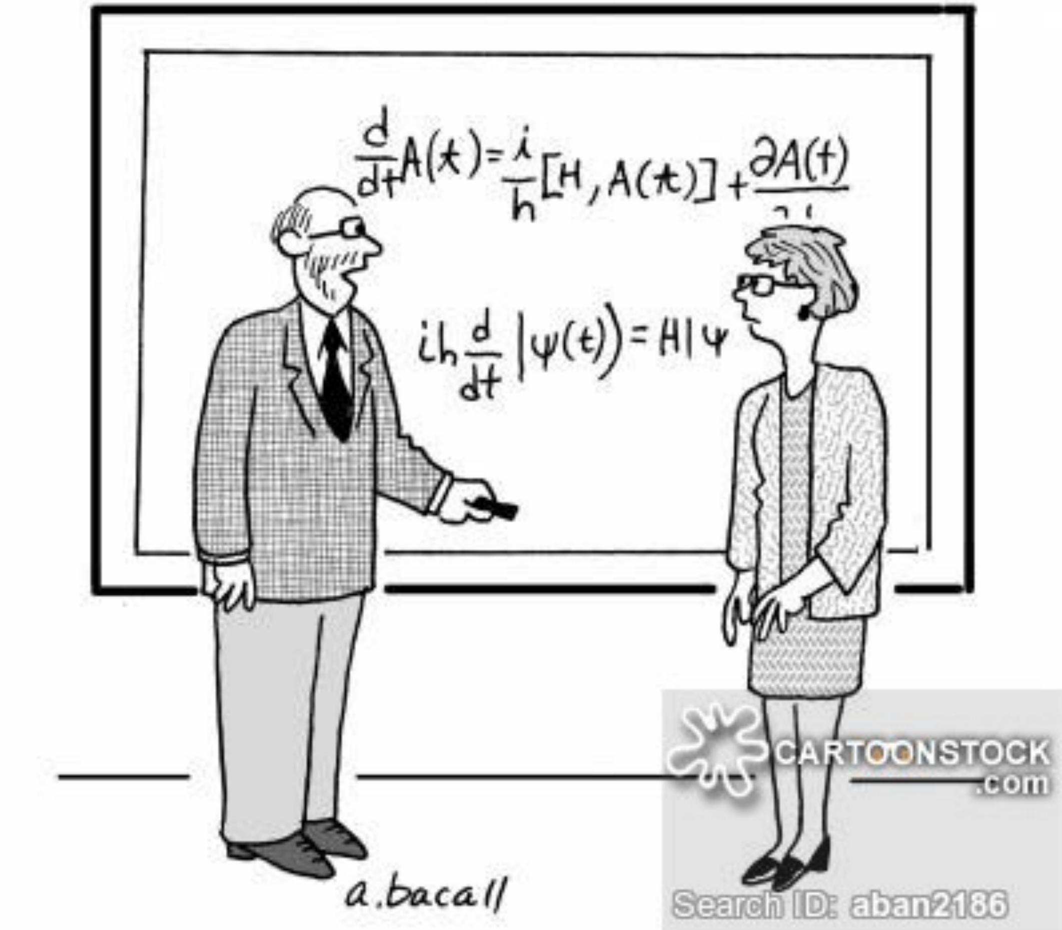
(Communicated by R. H. Fowler, F.R.S.—Received March 12, 1929.)

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

Anyways…

………the difficulty is only that the exact application of these laws leads to equations much too complicated to be soluble.



"I can understand Heisenberg's equation and Schrodinger's equation for quantum mechanics but I cannot understand derivative trading."

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

Dirac's Challenge

We know it right!

The general theory of quantum mechanics is almost complete……The underlying laws necessary for the mathematical theory of large parts of physics and the whole of chemistry are thus completely known…

…..And therefore approximate practical methods of applying QM should be developed.

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Chemistry is not just test tubes and chemicals. In electronic structure theory, quantum mechanics is used to compute the structure and properties of atoms, molecules, surfaces and solids and their interaction.

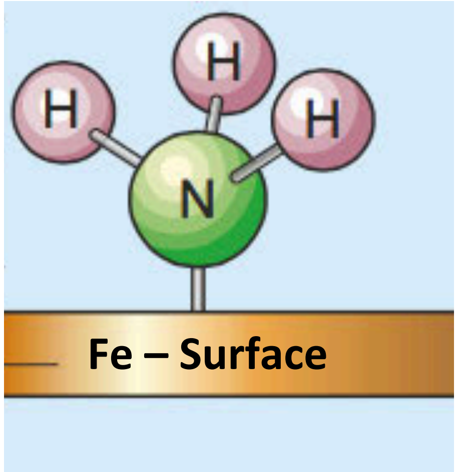
Course of chemical reactions – Structure and Reactivity at T → 0K and T> 0K

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

$$k = k_0 e^{-E^*/RT}$$

Returning to the problem at hand….

$$N_2 + 3H_2 \rightarrow 2NH_3.$$



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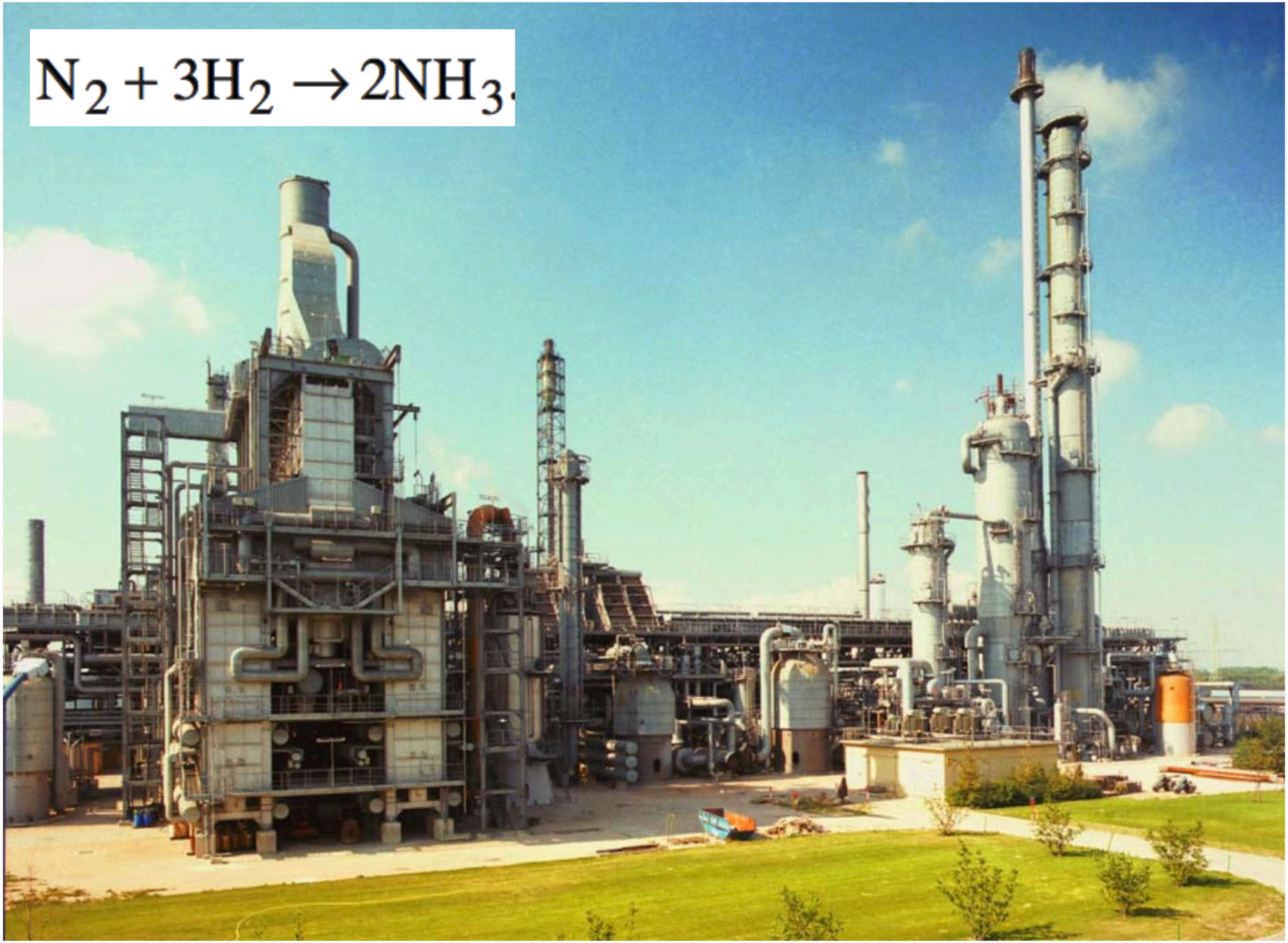
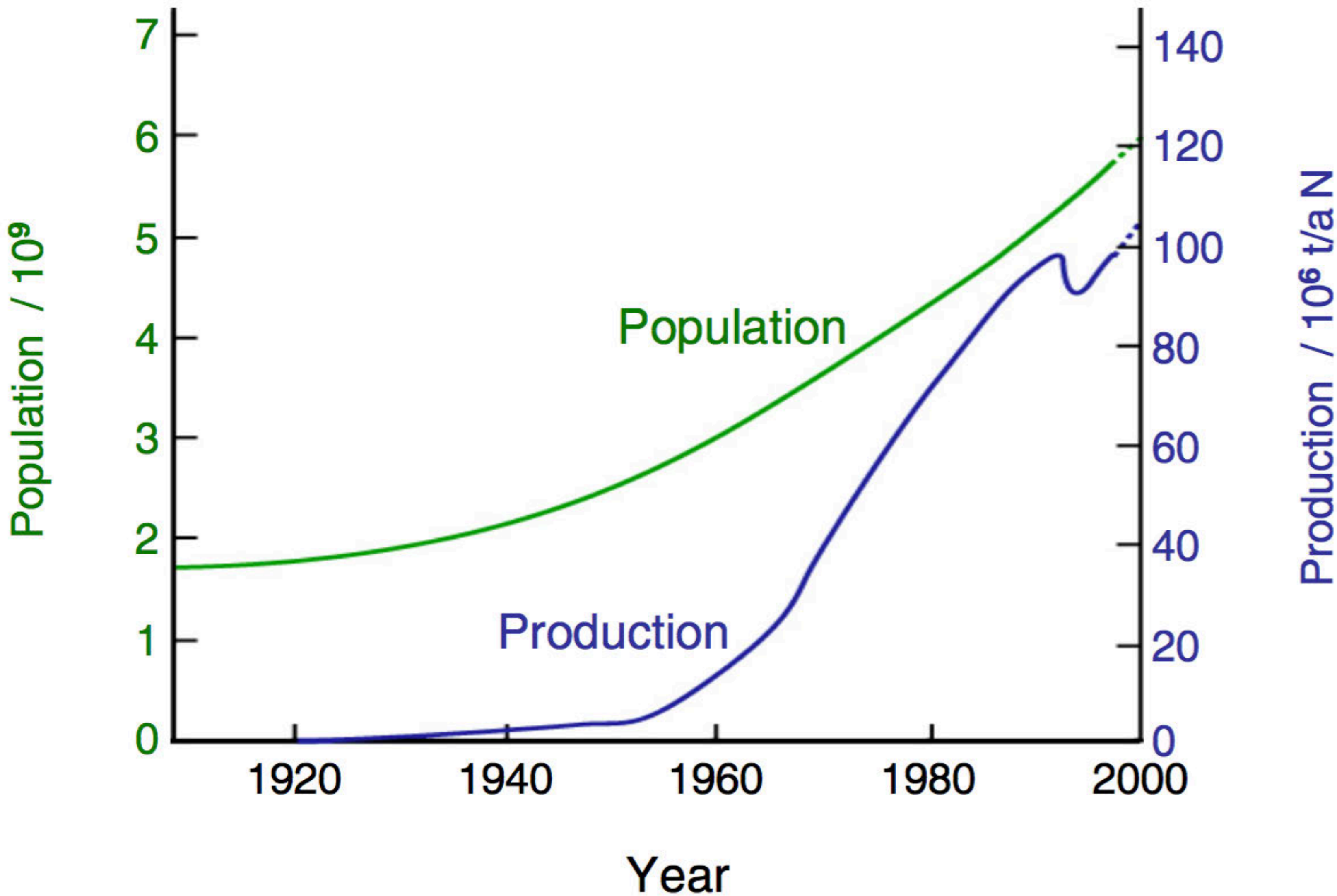


The best identified materials, practical rates are only attainable at elevated temperatures (700 K) and pressures (100 atm).

World population and ammonia production



N2 forms about 78% of Earth's atmosphere!

Nitrogen fixation means transformation of the abundant N_2 molecule (which constitutes about 80% of our air) from its state of very strong bond between the two N atoms into a more reactive form according to the reaction $N_2 + 3H_2 \rightarrow 2NH_3$. This reaction of ammonia formation could be realized in 1909 by F. Haber (Nobel Prize 1919) in the laboratory by the use of an osmium catalyst in a high pressure flow apparatus [6]. C. Bosch (Nobel Prize 1931) from the BASF company started immediately to transform this process into technical scale, and the first industrial plant started operation in 1913, only a few years later. Fig. 3 shows the growth of the world population together with the ammonia production over the last century [7], and it is quite obvious that our present life would be quite different without the development of the Haber-Bosch process.

One of the first and still most important technical applications of this principle was realized about 100 years ago: Due to the continuous increase of the world population and the exhaust of the natural supply of nitrogen fertilizers the world was facing a global threat of starvation. As Sir William Crookes, president of the British Association for the advancement of sciences, formulated it [8]: "… *all civilized nations stand in deadly peril of not having enough to eat. … the fixation of atmospheric nitrogen is one of the great discoveries awaiting the ingenuity of chemists*".

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Nitrogen is the most abundant element in the earth's atmosphere, and its conversion to ammonia is one of the highest volume industrial reactions. NH_3 is primarily used in fertilizers and also acts as a precursor to several other important chemicals such as nitric acid. NH_3 is also being considered as a carbon-free future fuel alternative.[1] Industrially, NH_3 is produced through the Haber Bosch (HB) process in which gaseous nitrogen and hydrogen react over an iron/ruthenium-based catalyst. The HB process is one of the most energy intensive chemical processes, consuming approximately 1%–1.5% of world energy.[2] By contrast, natural nitrogen fixation by diazotrophs, principally an electrochemical NH_3 synthesis reaction, is much more energy efficient.[3] In a future with plentiful renewable electricity, an artificial electrochemical system to produce ammonia from nitrogen could be highly beneficial.

Possible heterogeneous catalysts for electrochemical nitrogen reduction (NRR) are currently marred by (1) the poor

However, large scale technical production would not have been possible without the availability of large quantities of a cheap catalyst. (The whole world supply of the precious metal osmium was only 80 kg in those days.) This task could be solved successfully by A. Mittasch [8] who in thousands of tests found that a material derived from a Swedish iron ore exhibited satisfactory activity. This type of doubly-promoted iron catalyst is in fact still in use today in almost all industrial plants.

Remarkably, despite the enormous technical significance of the Haber-Bosch reaction and despite of numerous laboratory studies its actual mechanism remained unclear over many years. P. H. Emmett, one of the pioneers of catalysis research, was honoured in 1974 by a symposium where he concluded at the end [9]: *"The experimental work of the past 50 years leads to the conclusion that the rate-limiting step in ammonia synthesis over iron catalysts is the chemisorption of nitrogen. The question as to whether the nitrogen species involved is molecular or atomic is still not conclusively resolved …"*.

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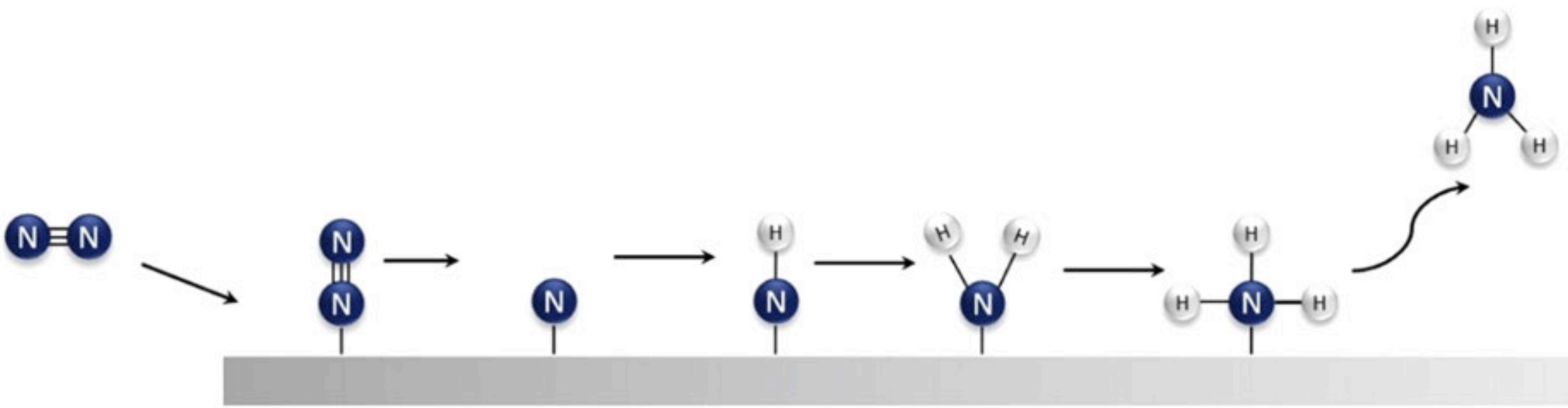

Returning to the problem at hand....

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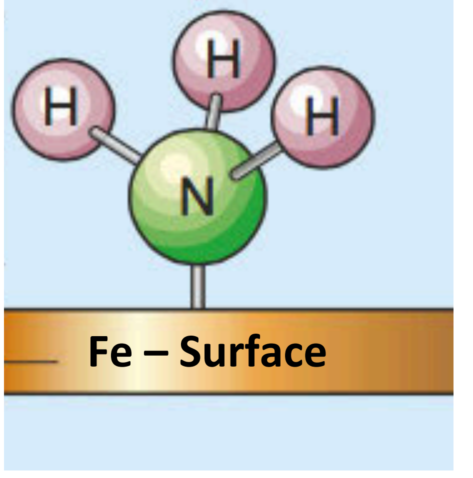


$$k = k_0 e^{-E^*/RT}$$

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

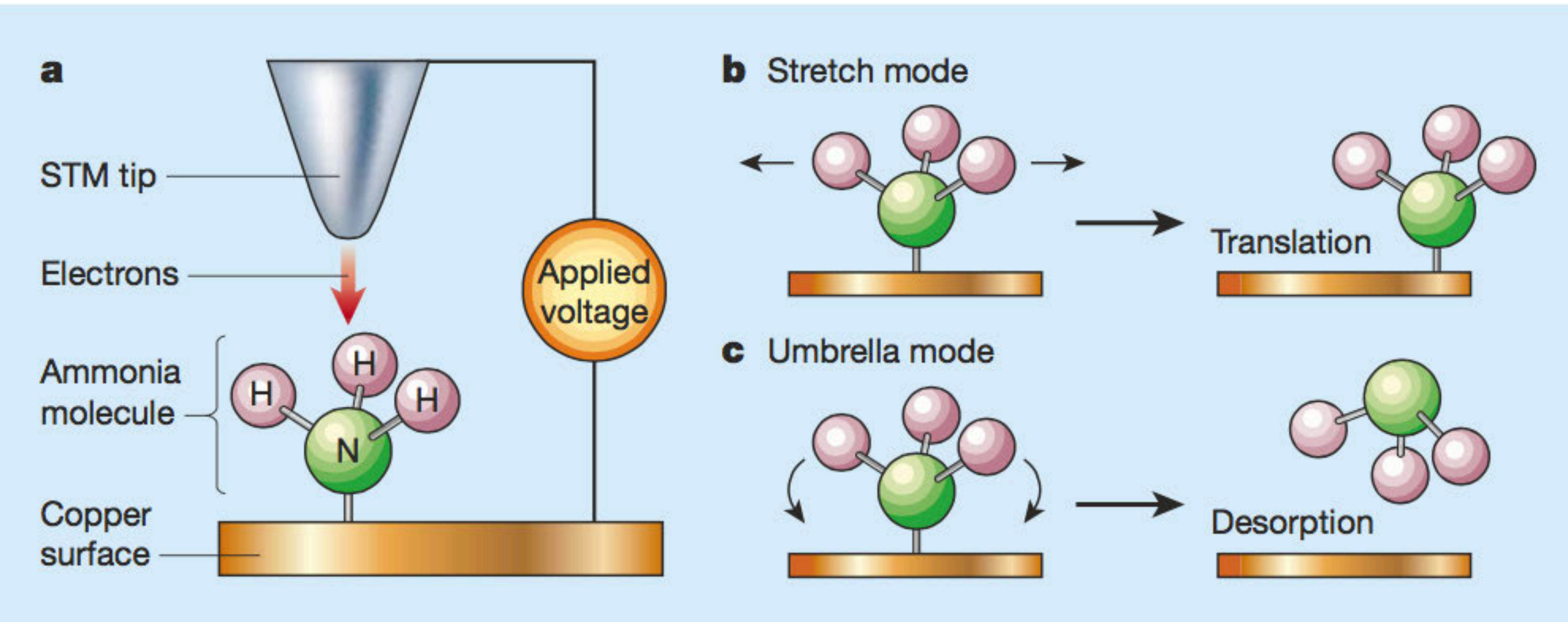
$$\hat{H} = -\frac{1}{2}\sum_{\alpha}\nabla_{\alpha}^2 - \frac{1}{2}\sum_{i}\nabla_{i}^2 + \frac{1}{2}\sum_{\alpha\neq\beta}\frac{Z_\alpha Z_\beta e^2}{R_\alpha - R_\beta} -$$

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

Chemical Reactivity…….

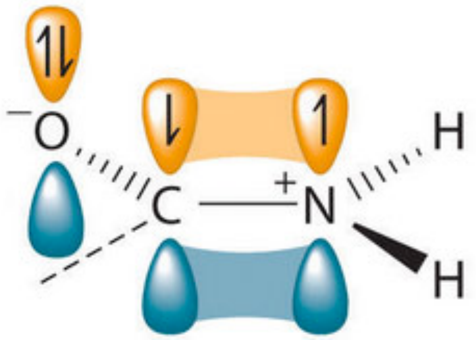
$$\hat{H}\psi(r) = E\psi(r)$$

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

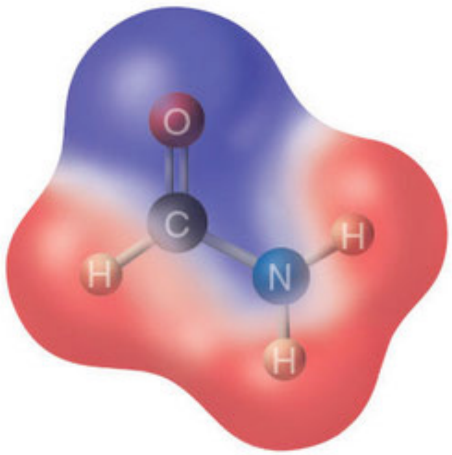


Chemical Reactivity…….

$$\psi(r) = \sum_{\mu=1}^{K} C_{\mu i} \tilde{\chi}_{\mu}$$



$$\rho = \sum_{i=1}^{n_{occ}} n_i |\psi_i|^2$$



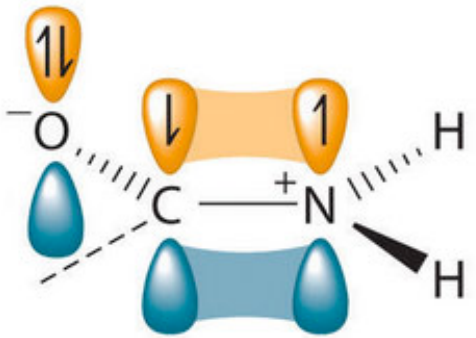
…….. DFT

For example….

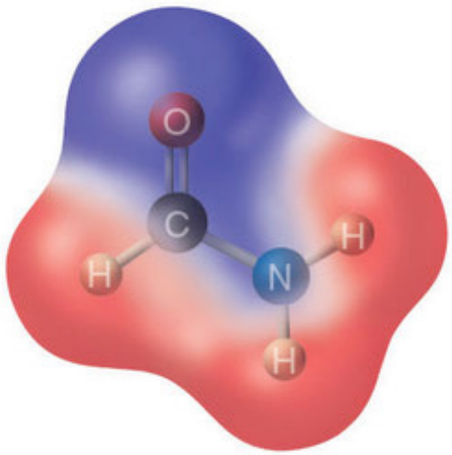
We shall return to this

Chemical Reactivity…….

$$\psi(r) = \sum_{\mu=1}^{K} C_{\mu i} \tilde{\chi}_{\mu}$$



$$f(r) = \left(\frac{\partial \rho(r)}{\partial N} \right)_{v(r)}$$



Fukui function / Index

For example….

We shall return to this

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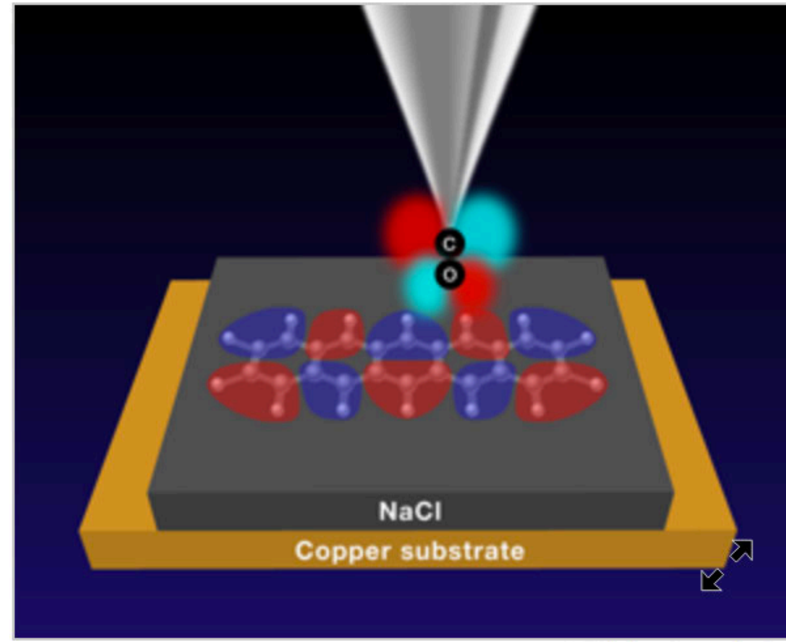

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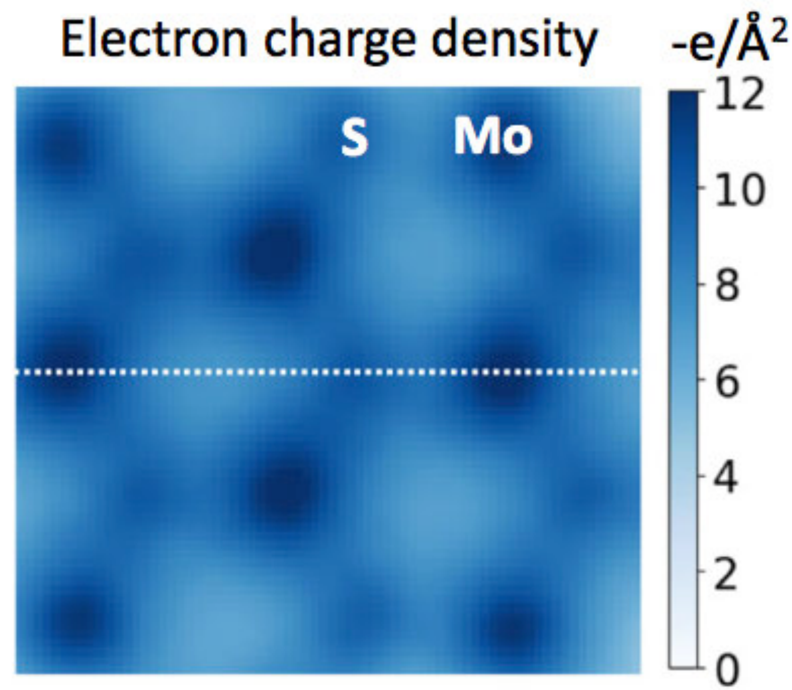

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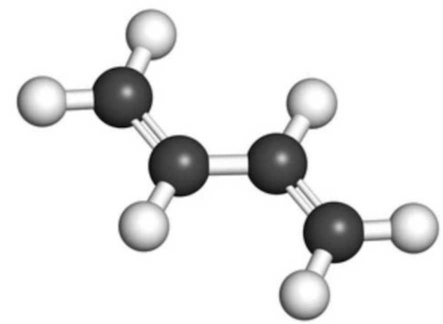
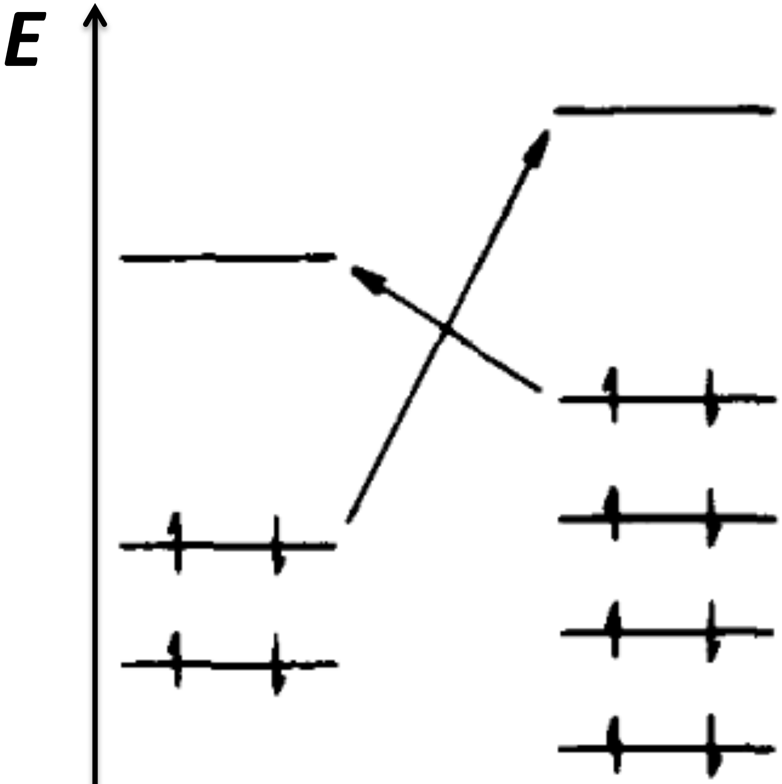
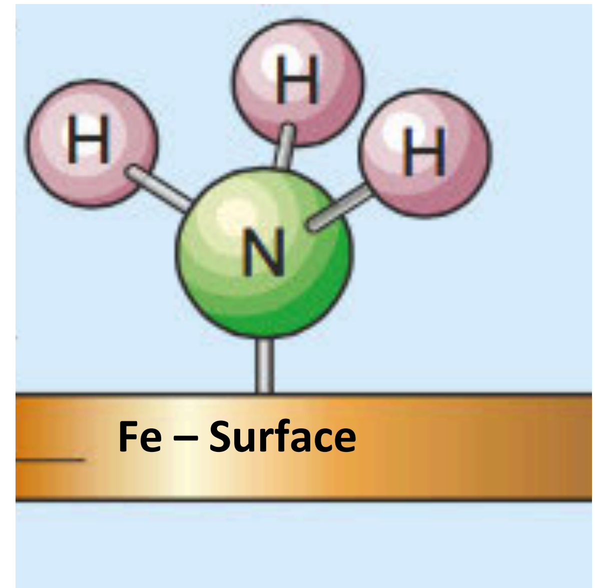


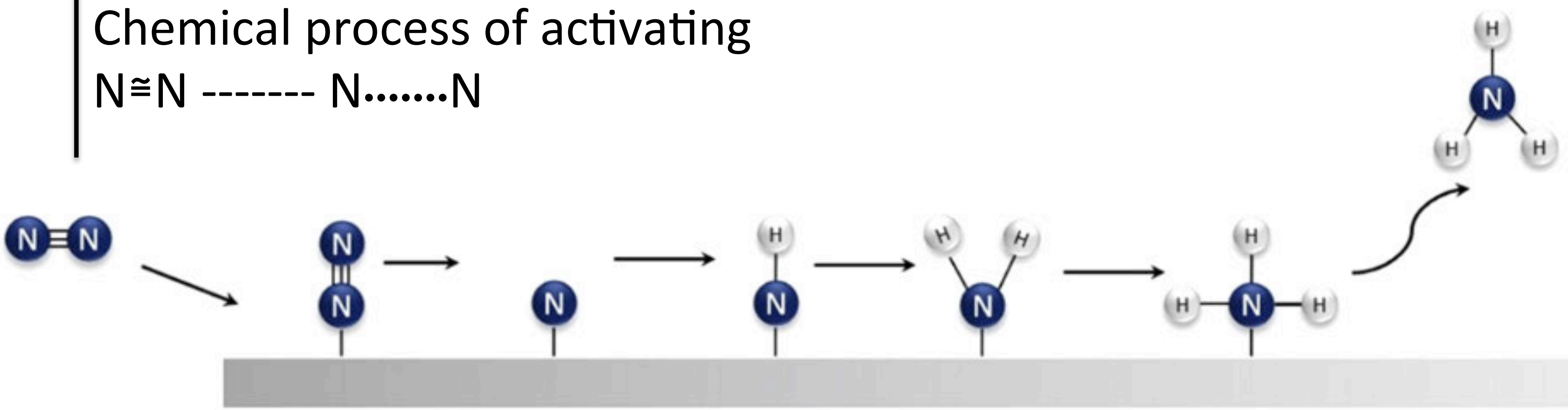
$$\psi_1 = 0.372\phi_1 + 0.602\phi_2 + 0.602\phi_3 + 0.372\phi_4$$
$$\psi_2 = 0.602\phi_1 + 0.372\phi_2 - 0.372\phi_3 - 0.602\phi_4$$
$$\psi_3 = 0.602\phi_1 - 0.372\phi_2 - 0.372\phi_3 + 0.602\phi_4$$
$$\psi_4 = 0.372\phi_1 - 0.602\phi_2 + 0.602\phi_3 - 0.372\phi_4$$





Chemical process of activating

N≅N ------- N.......N



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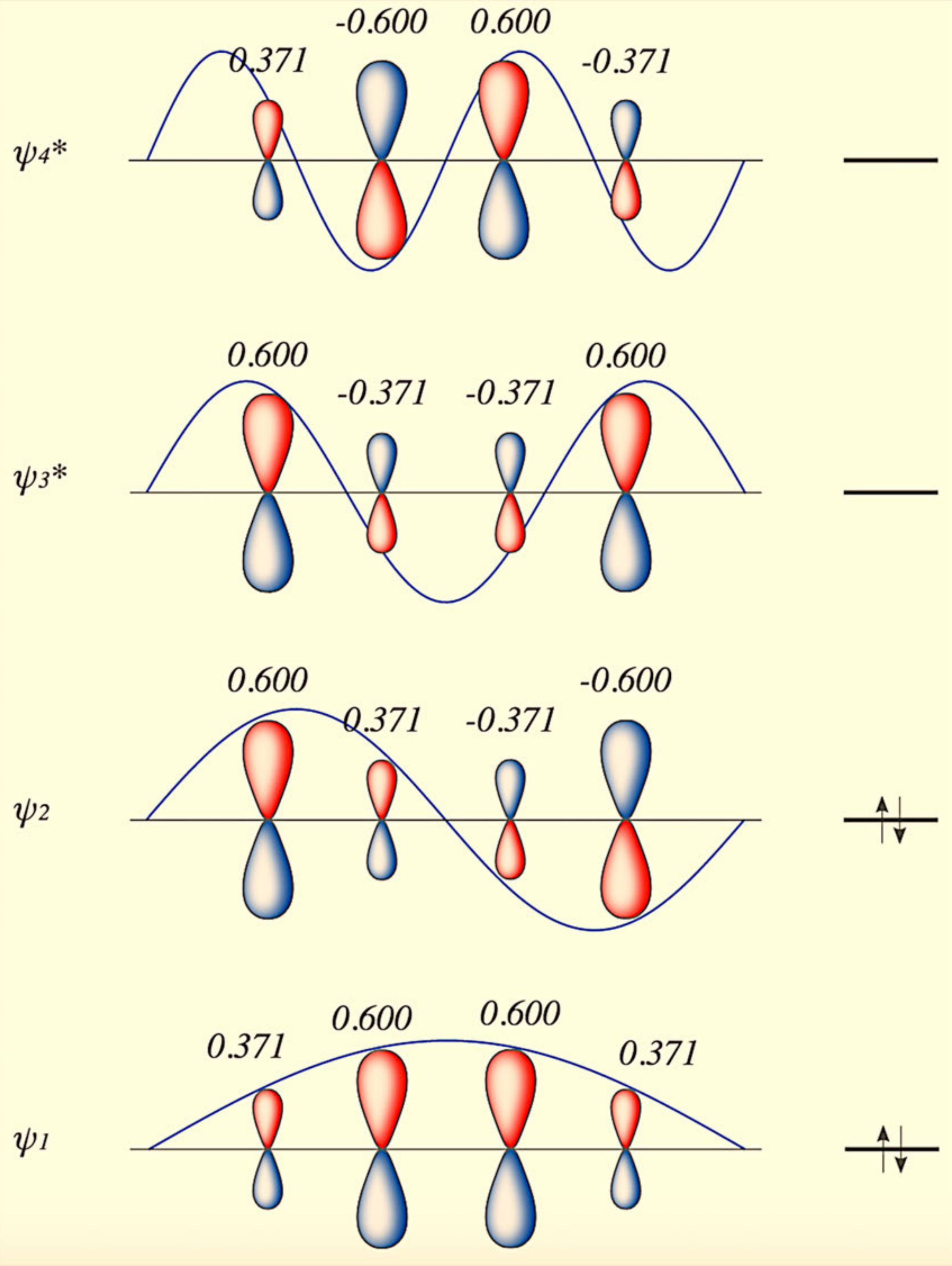
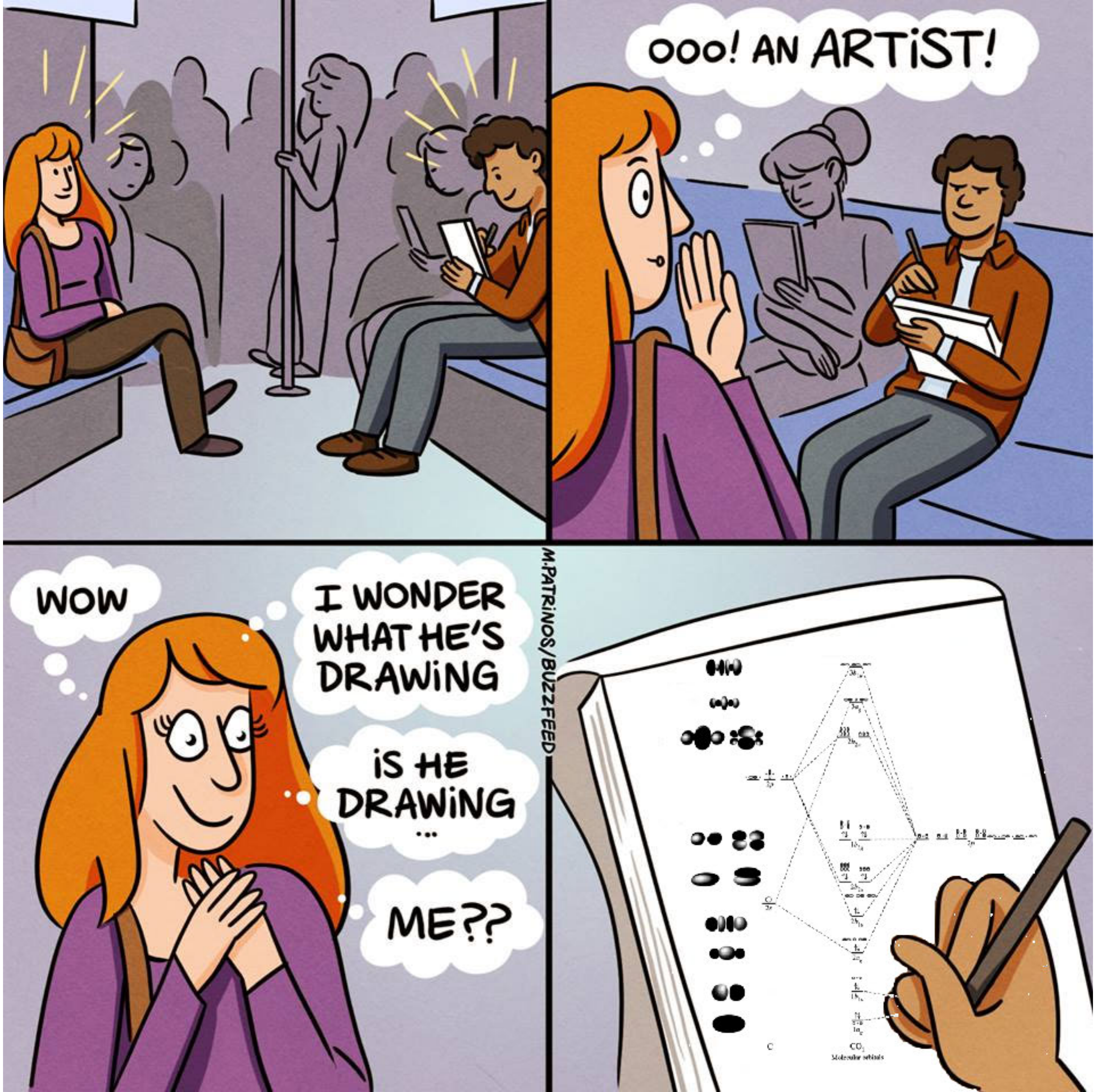
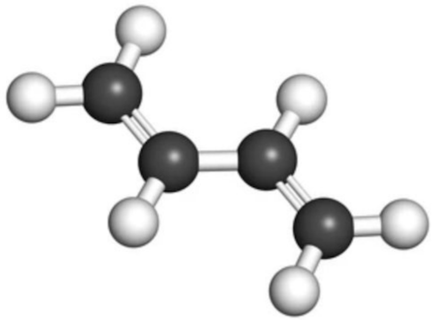
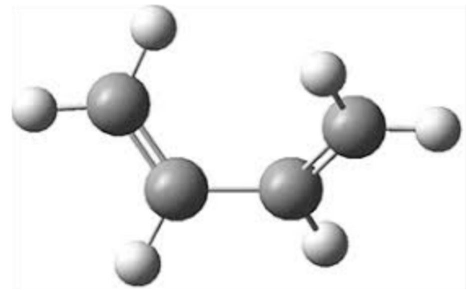
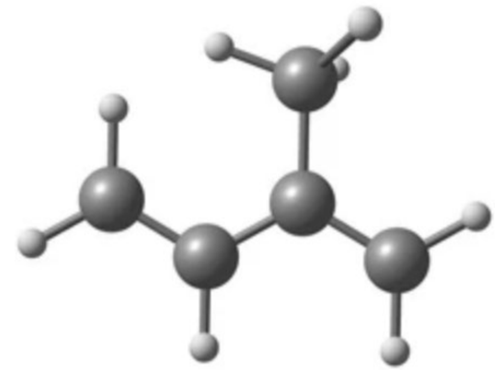


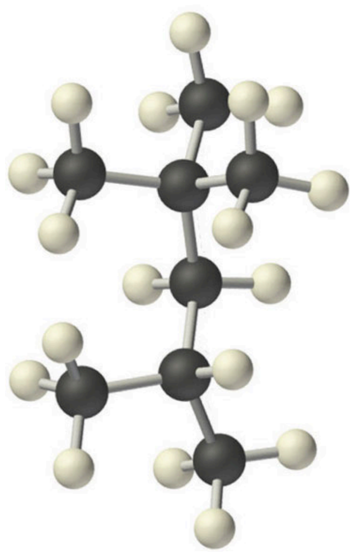

OOO! AN ARTIST!
WOW
I WONDER WHAT HE'S DRAWING
IS HE DRAWING ...
ME??
M.PATRINOS/BUZZFEED

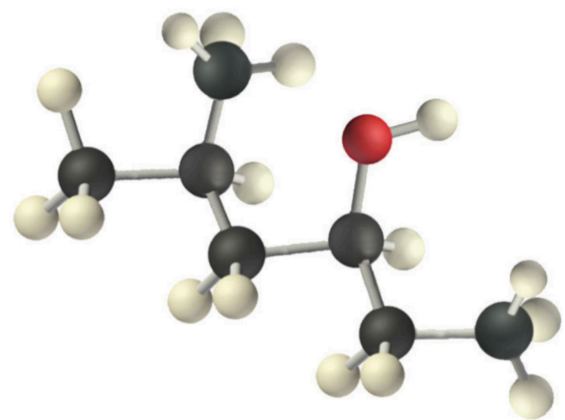
Chemical Reactivity…….











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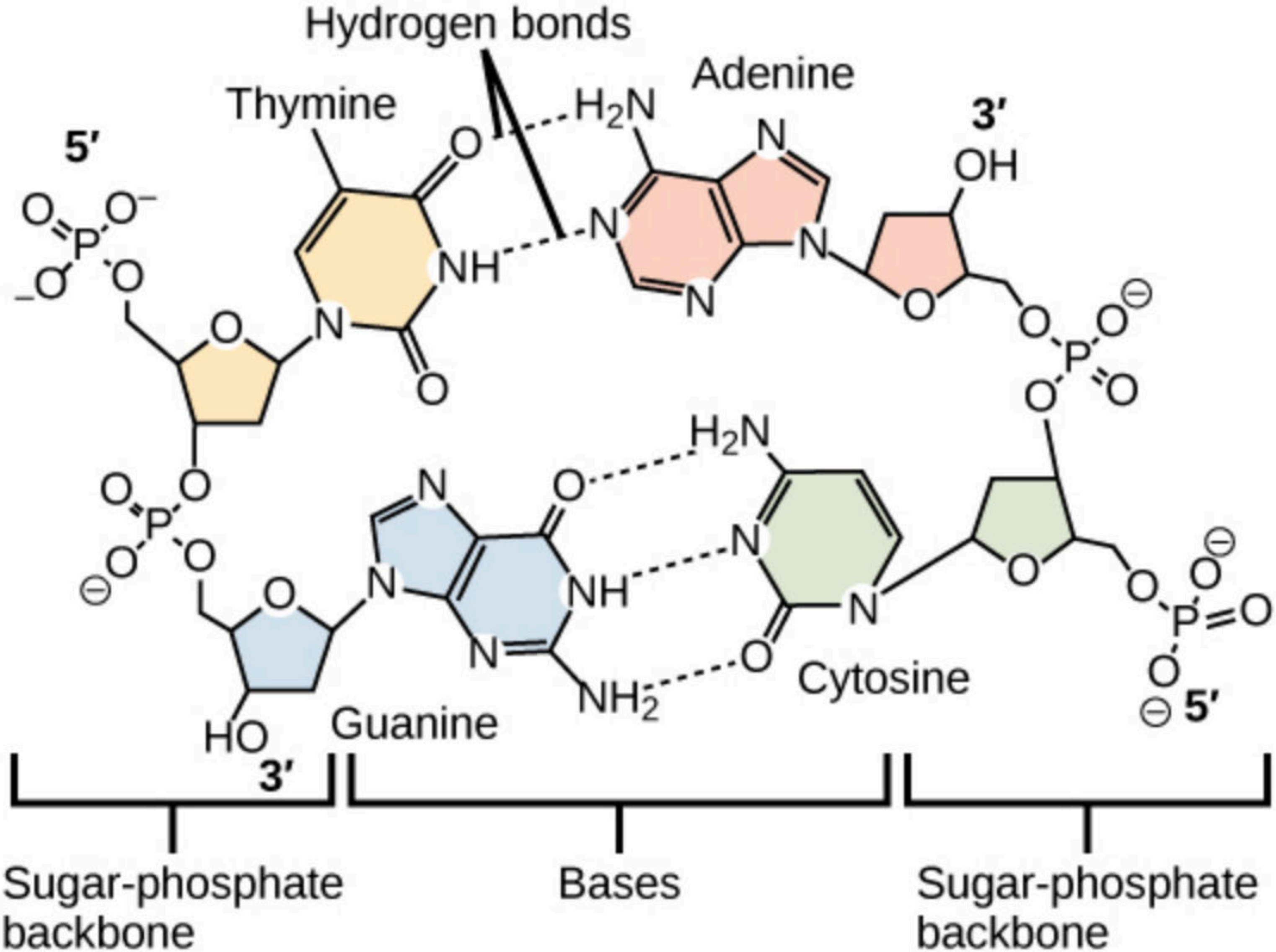

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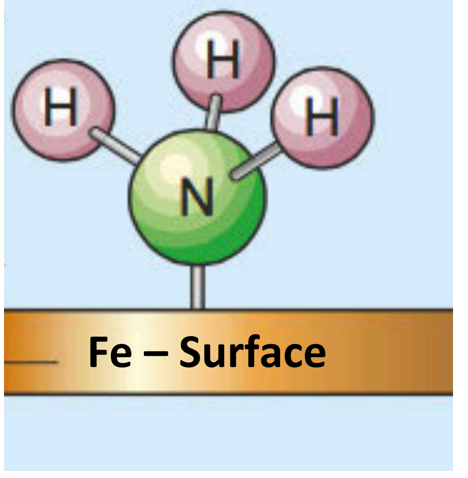

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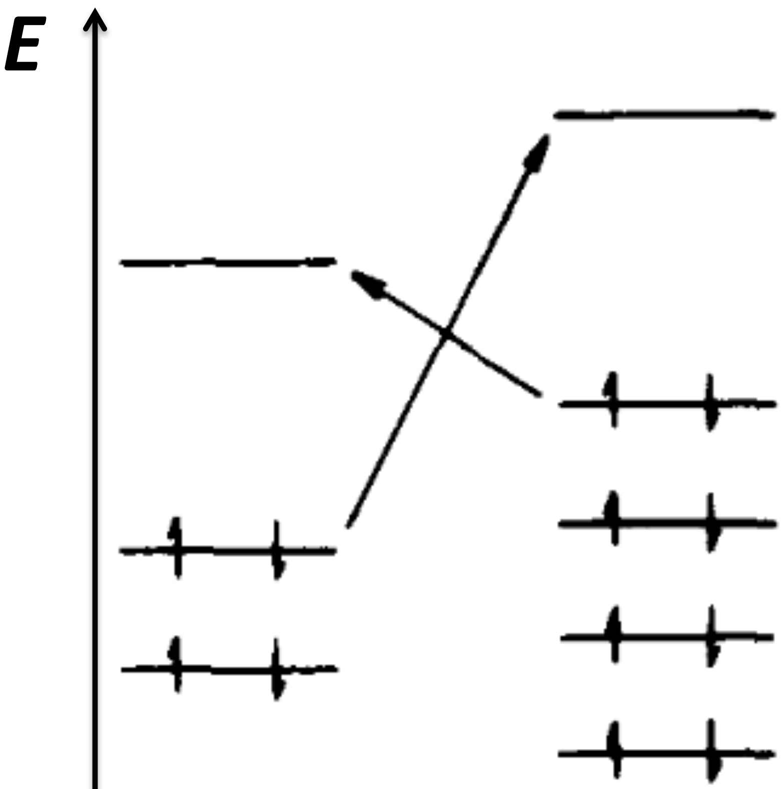

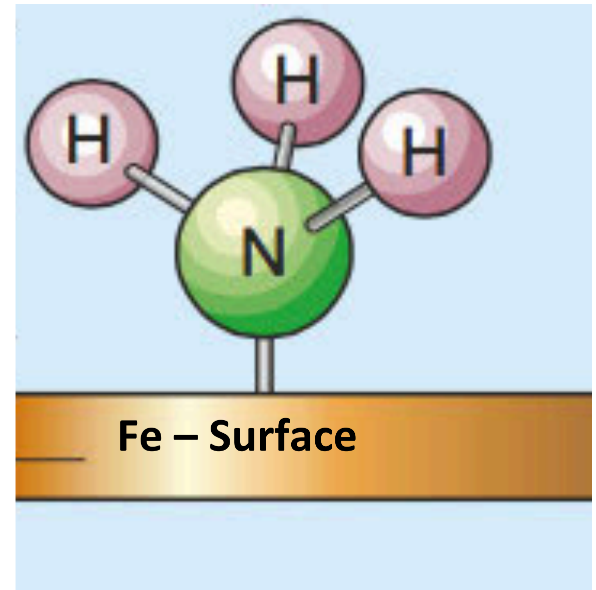

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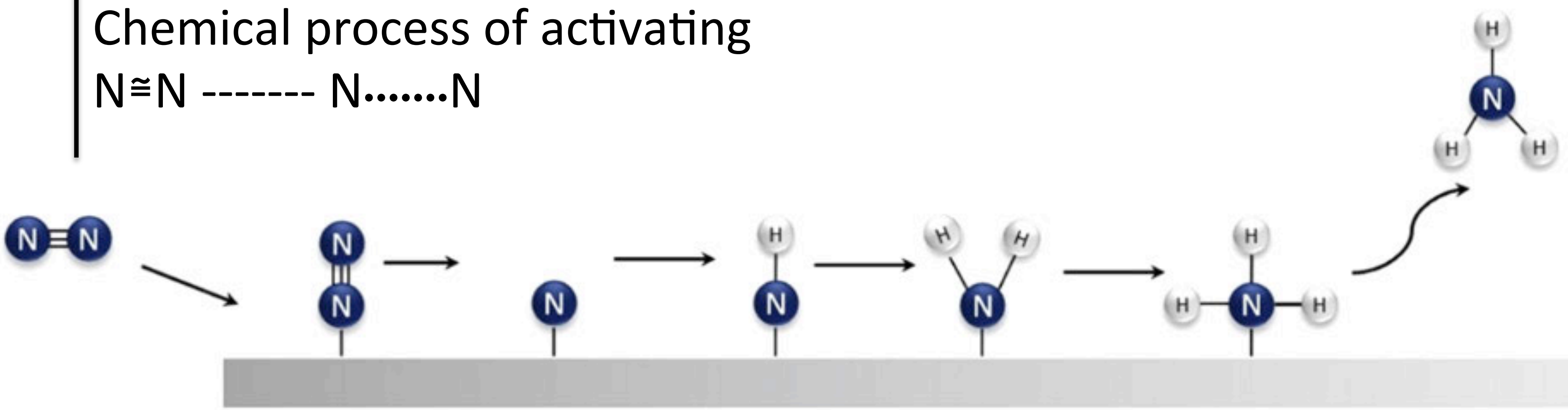
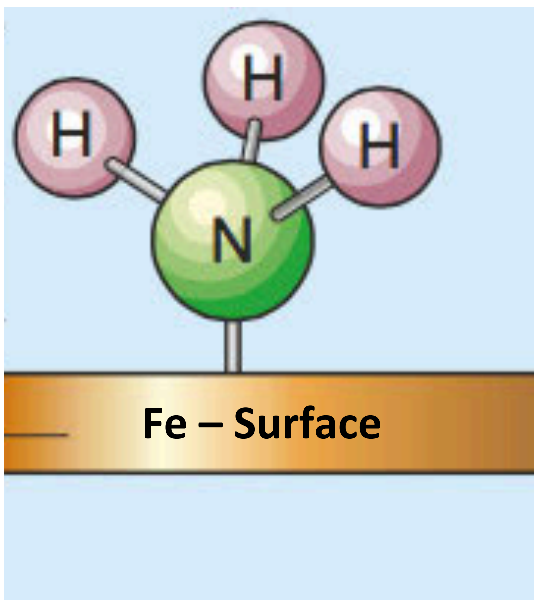
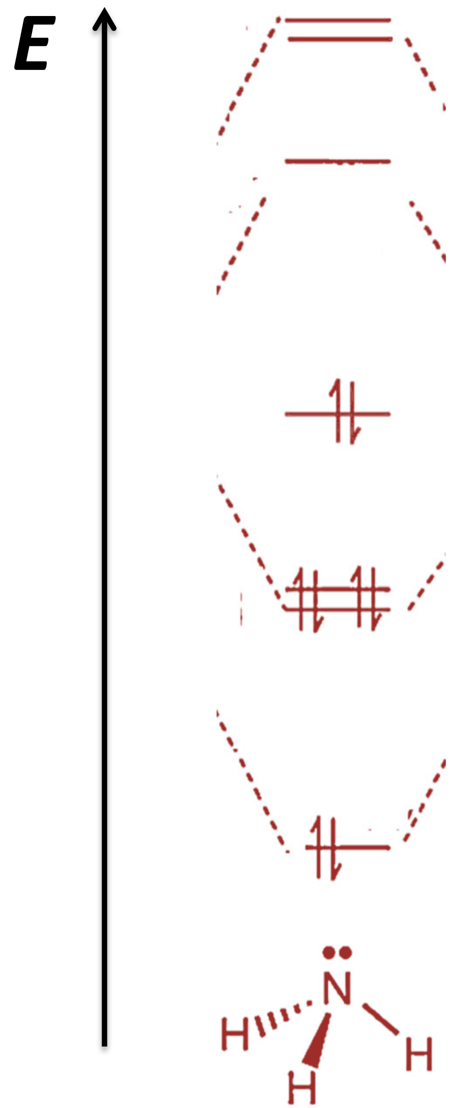
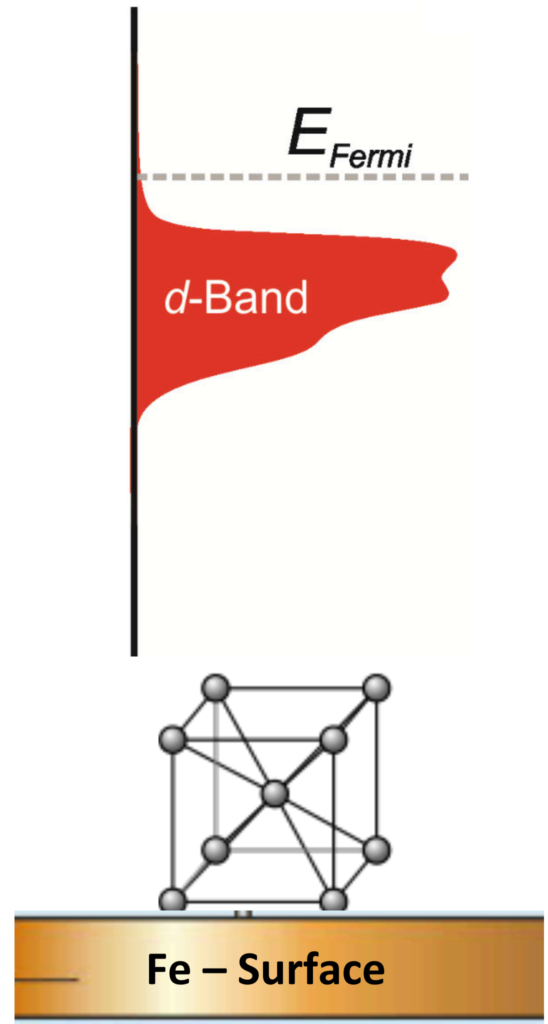


Chemical processes .....

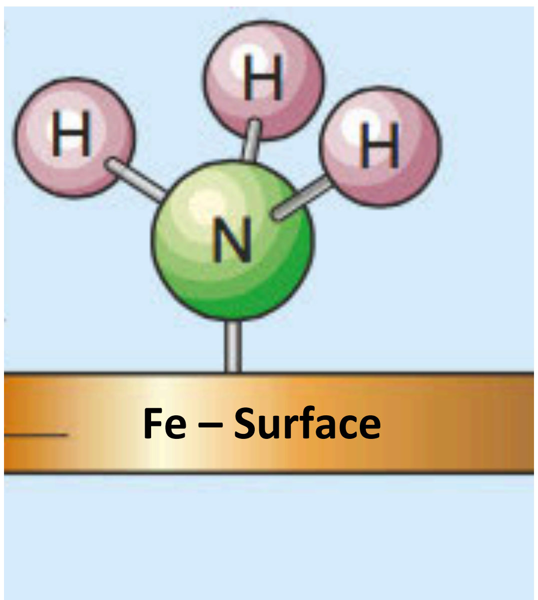


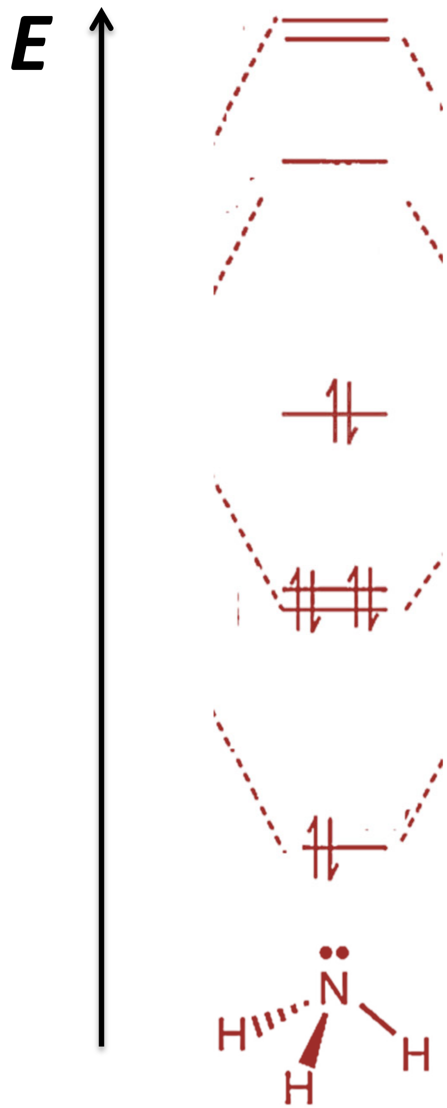


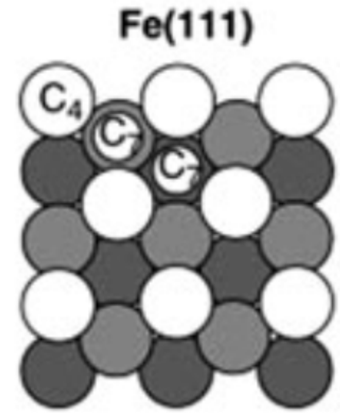


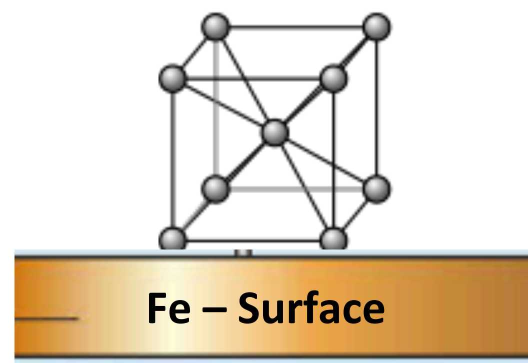
Schematic

Chemical processes .....









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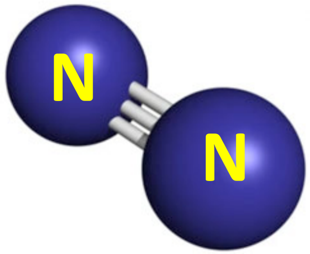
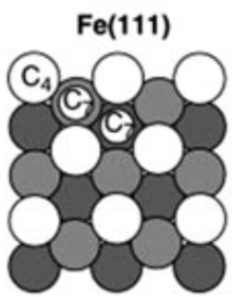


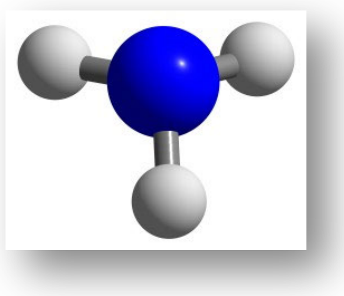
$$\psi(r) = E\psi(r)$$

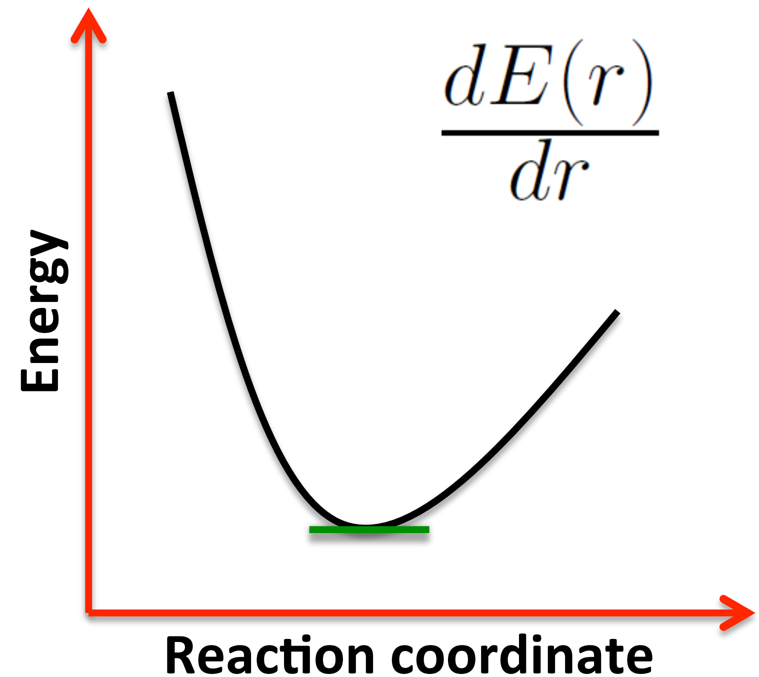


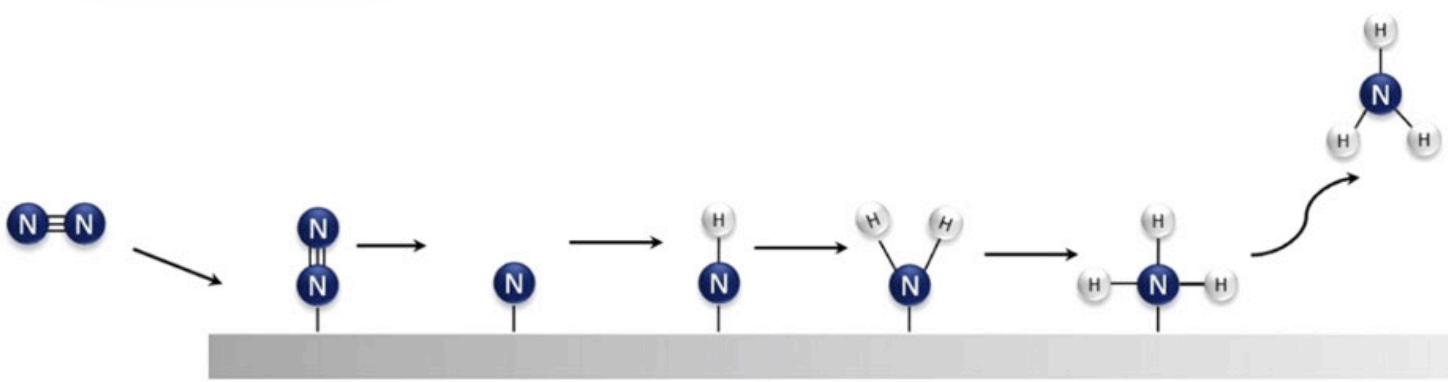
$$\psi(r) = E\psi(r)$$

Energies & Forces

Is the structure/geometry in equilibrium?

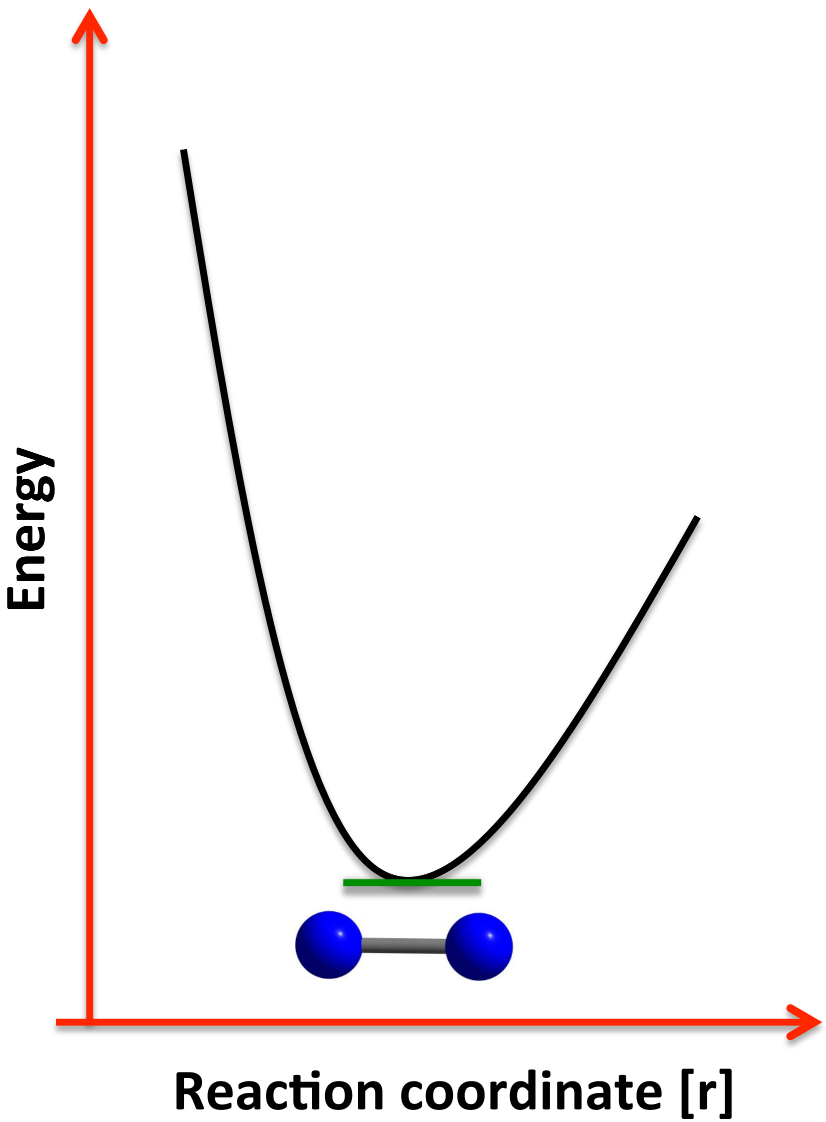


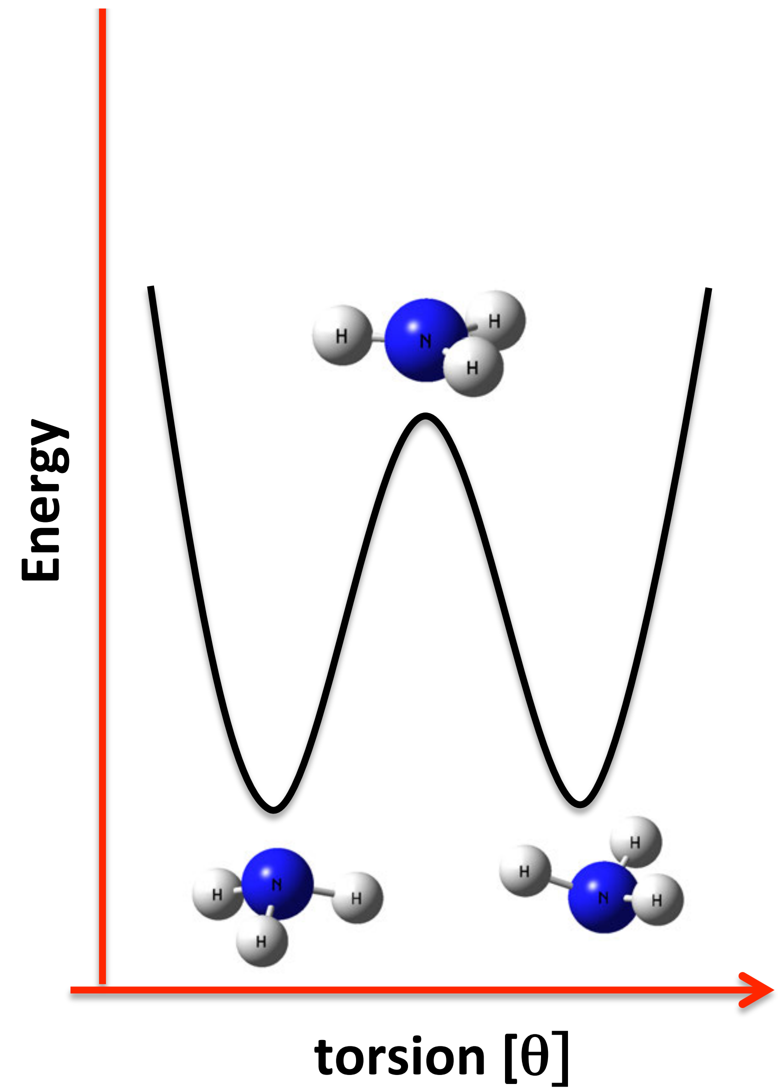


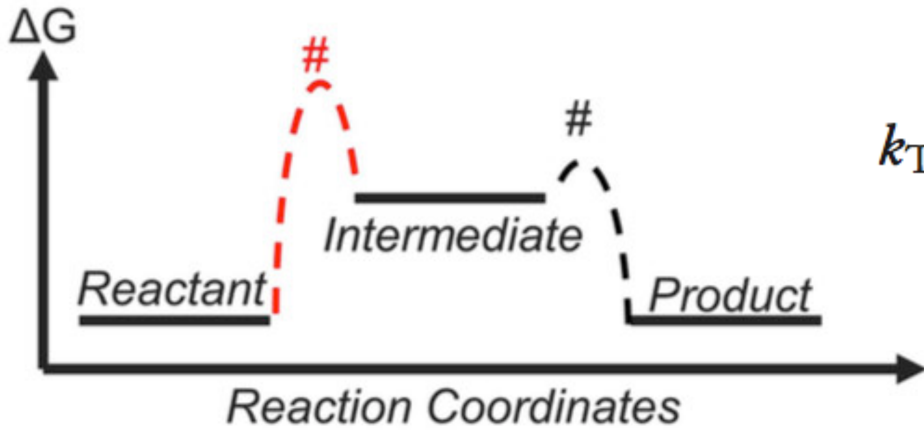


$$\hat{H}\psi(r) = E\psi(r)$$

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

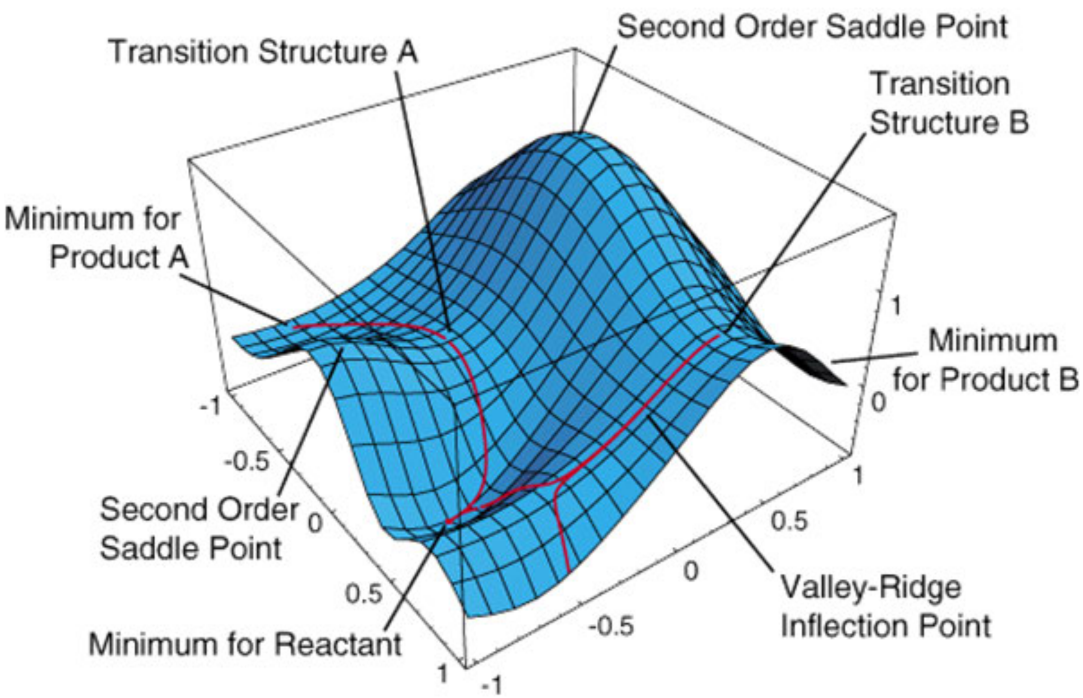


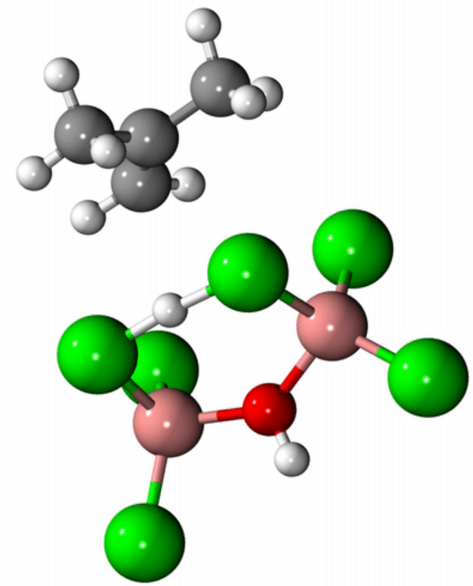




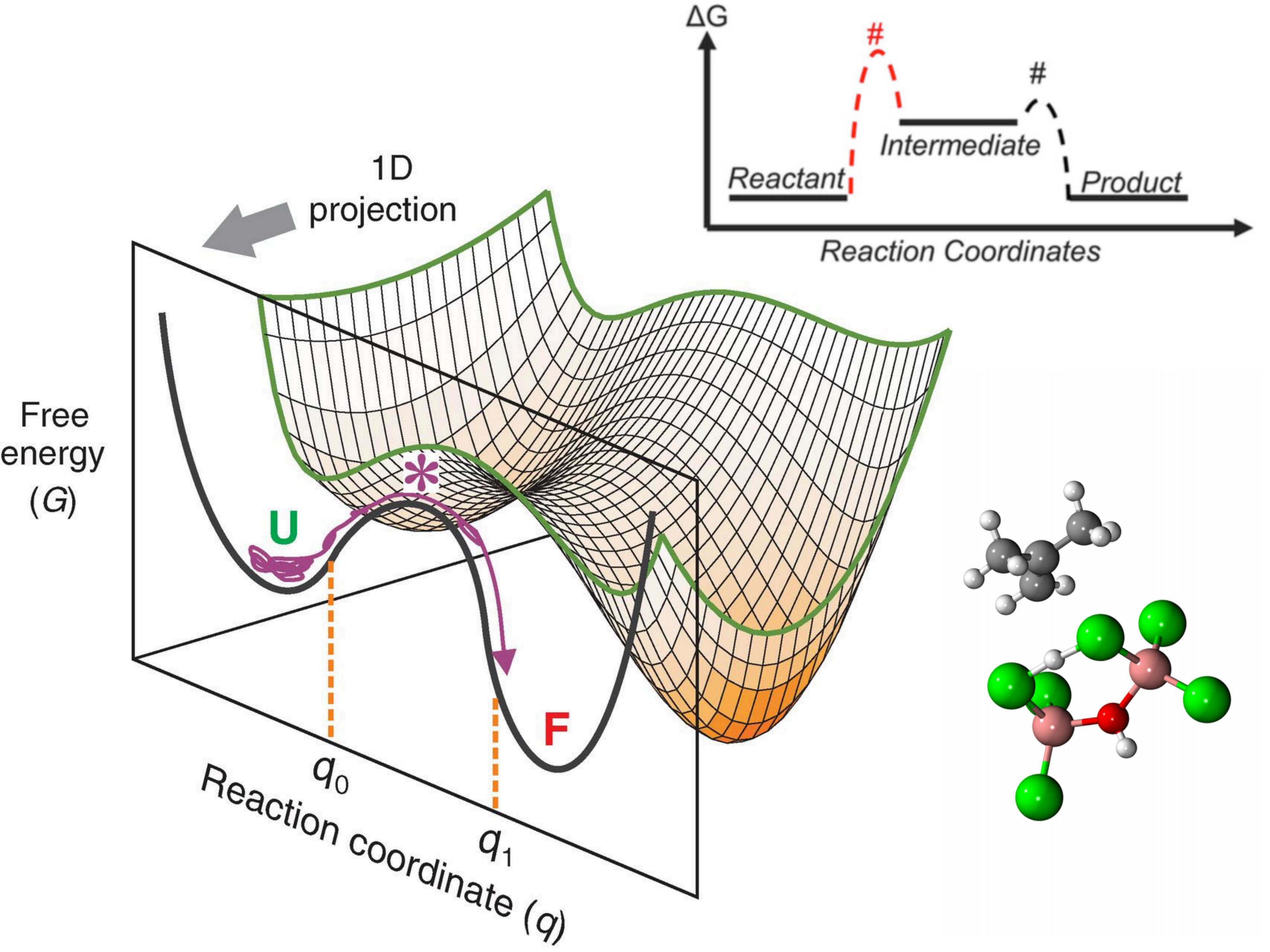
$$k_{\mathrm{TST}} = \frac{k_{\mathrm{B}} T}{h} (c^{\mathrm{o}})^{\Delta \nu^{\dagger}} \exp\left(-\frac{\Delta G^{\mathrm{o}\dagger}}{RT}\right)$$

$$\Delta E_{\mathrm{a}} = E_0 + \alpha \Delta H$$





Course of chemical reactions – Structure and Reactivity
at T → 0K and T> 0K



ΔG
#
#
Intermediate
Reactant
Product
Reaction Coordinates
1D
projection
Free
energy
(G)
U
*
F
q0
q1
Reaction coordinate (q)