COMPUTATIONAL MODELING OF NANOSCOPIC PROCESSES

A way of thinking

Con un ángel amarillo
y un sinsonte de papel,
pasa envuelto en suave brillo
Víctor Manuel.

Entre un ángel amarillo
y un sinsonte de papel
yace envuelto en suave brillo
Víctor Manuel.

Nicolás Guillén

Luis A. Montero
Universidad de La Habana, Cuba

Sizes and scales

Sizes and scales

Sizes and Scales in Nature

We **humans develop knowledge** and the perception of the surrounding universe **from our standing point and our dimensions**.

Sizes and Scales in Nature

Science is essentially a systemic assembling of knowledge. Consequently, it **was also founded on our perception of the world at our scale**.

Sizes and Scales in Nature

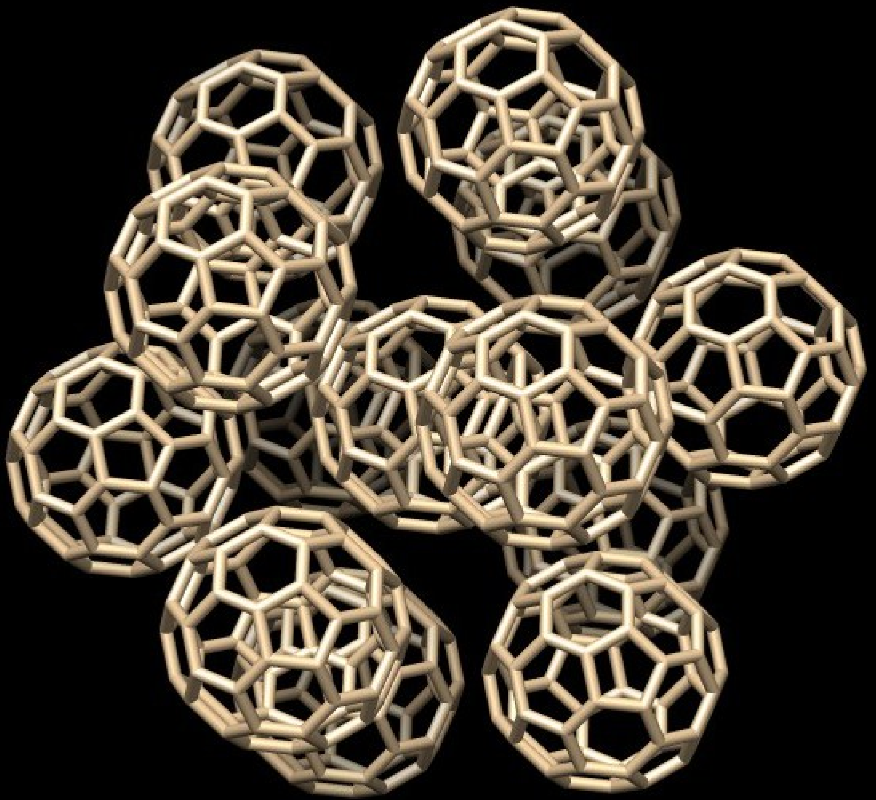
- We also created space measurements at our scale.

Sizes and Scales in Nature

- We also created space measurements at our scale.
- **SI** space unit is meter and a person could range between 1 and 2 m tall.

Length	Area	Scale name
< 1 μm	< 1 μm²	Nanoscopic
1 μm – 1 mm	1 μm² – 1 mm²	Microscopic
1 mm – 1 m	1 mm² – 1 m²	Personal
1 m - 1 km	1 m² - 1 km²	Local
1 km - 100 km	1 km² - 10 000 km²	Regional
100 km - 10 000 km	10 000 km² - 100 000 000 km²	Continental
> 10 000 km	>100 000 000 km²	Global

Including scales and sizes in our **way of thinking** helps for better understanding our natural surrounding.



Models and modeling in the nanoworld

What is a model?

- A **model** *is a representation of any object, made or created for a given purpose*.

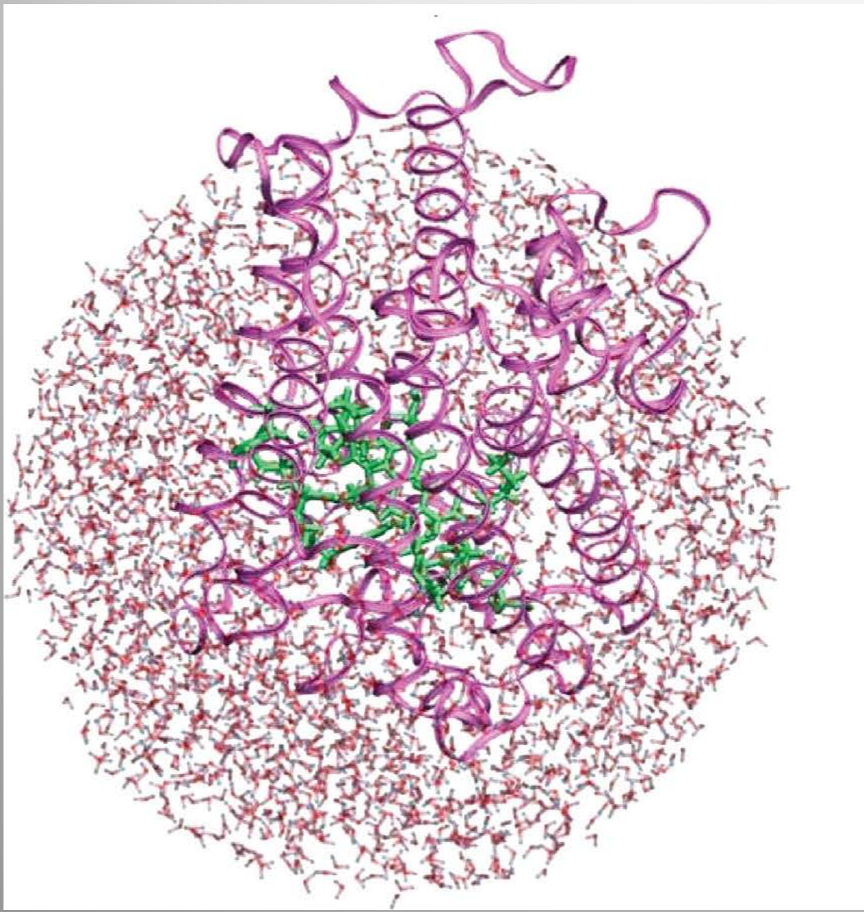
- The *Encyclopædia Britannica* understands a model as *a description or analogy used for aiding visualization of something (as could be an atom) that can not be directly observed.*

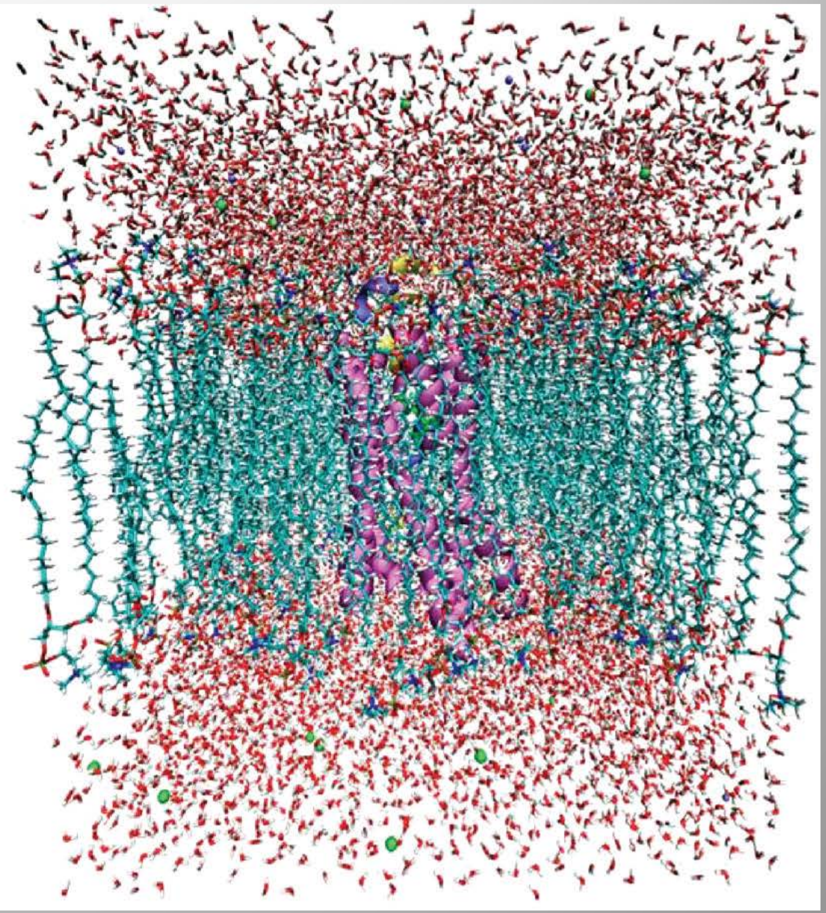
What is a model?

•A **model** *is a representation of any object, made or created for a given purpose*.

•The *Encyclopædia Britannica* understands a model as *a description or analogy used for aiding visualization of something (as could be an atom) that can not be directly observed*.

Rhodopsin structures after molecular dynamics simulations.





a) explicit solvent; **b) rhodopsin / membrane / water / ions**

Modelación Molecular de Rodopsinas Humanas Mutantes asociadas a Retinosis Pigmentaria.. Tesis presentada en opción al grado científico de Doctor en Ciencias Médicas.,Erix Wiliam Hernández Rodríguez., Universidad de Ciencias Médicas de La Habana, La Habana, 2013

Modeling at Nanoscales

The fundamental purpose of “molecular” or “nanoscale modeling” is ***building virtual models on structures and processes occurring mostly at dimensions around 10^{-9} m that were both perceptible and reliable.***

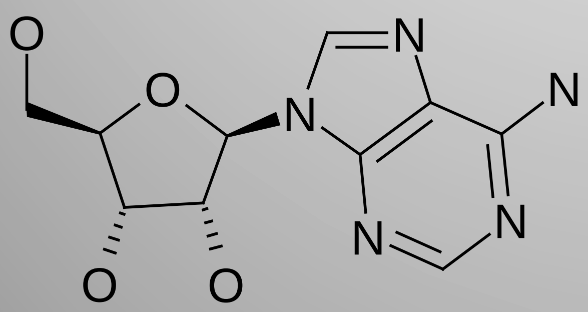
Nanoscale modeling works with tools developed by mathematics, chemistry, physics and computer sciences.

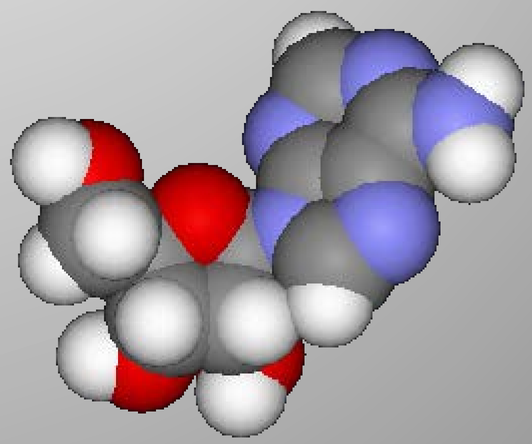
Modeling at Nanoscales

The fundamental purpose of “molecular” or “nanoscale modeling” is ***building virtual models on structures and processes occurring mostly at dimensions around 10^{-9} m that were both perceptible and reliable.***

Nanoscale modeling works with tools developed by mathematics, chemistry, physics and computer sciences.

Computer representation of "nanoscopic" systems





Adenosine

What we represent?

Molecular modeling holds by representing molecular and crystal structures in computer output devices or any other information supporting material.

What we represent?

Molecular modeling holds by representing molecular and crystal structures in computer output devices or any other information supporting material.

Such structures are defined in terms of the relative positions of centers or typical reference points of the system components.

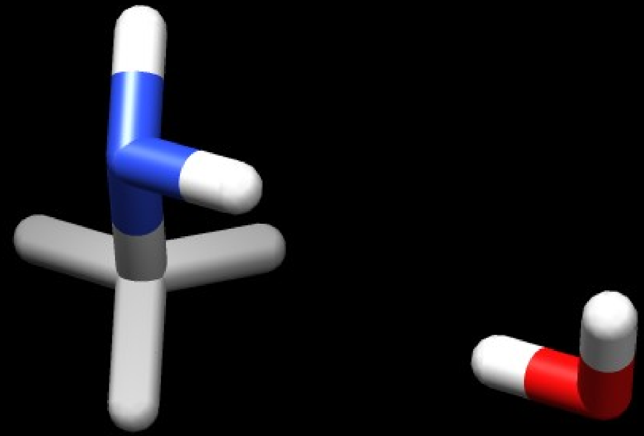
What we represent?

Molecular modeling holds by representing molecular and crystal structures in computer output devices or any other information supporting material.

Such structures are defined in terms of the relative positions of centers or typical reference points of the system components.

Centers are placed in coordinates that relate with the geometry of the nanoscopic system, either experimentally or theoretically obtained.

Methyl amine and water



Most extended forms of representation

Traditional models of ethane

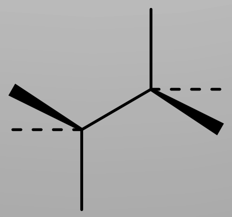
- C_2H_6, is a model of empirical formula based on stoichiometry.
- $H_3C\text{-}CH_3$ is a model of structural formula.
- The nearest approach to an structural representation is the "stick model":

Traditional models of ethane

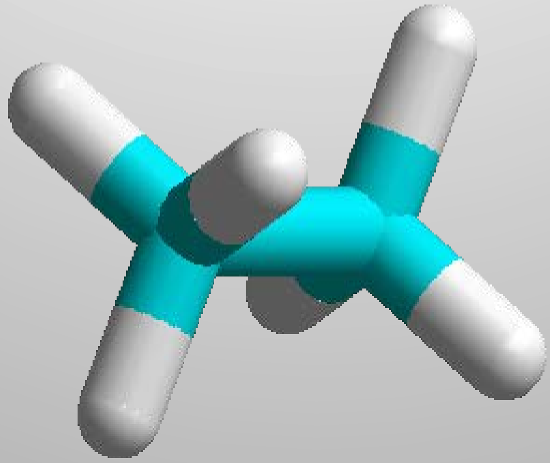
- C_2H_6, is a model of empirical formula based on stoichiometry.
- $H_3C\text{-}CH_3$ is a model of structural formula.
- The nearest approach to an structural representation is the “stick model”:

Traditional models of ethane

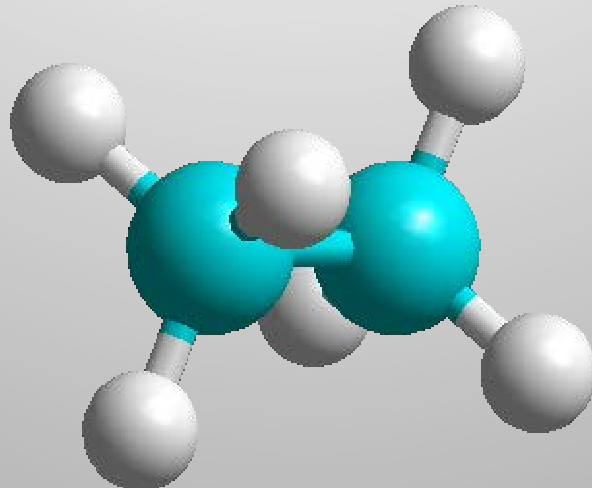
- C_2H_6, is a model of empirical formula based on stoichiometry.
- $H_3C\text{-}CH_3$ is a model of structural formula.
- The nearest approach to an structural representation is the “stick model”:



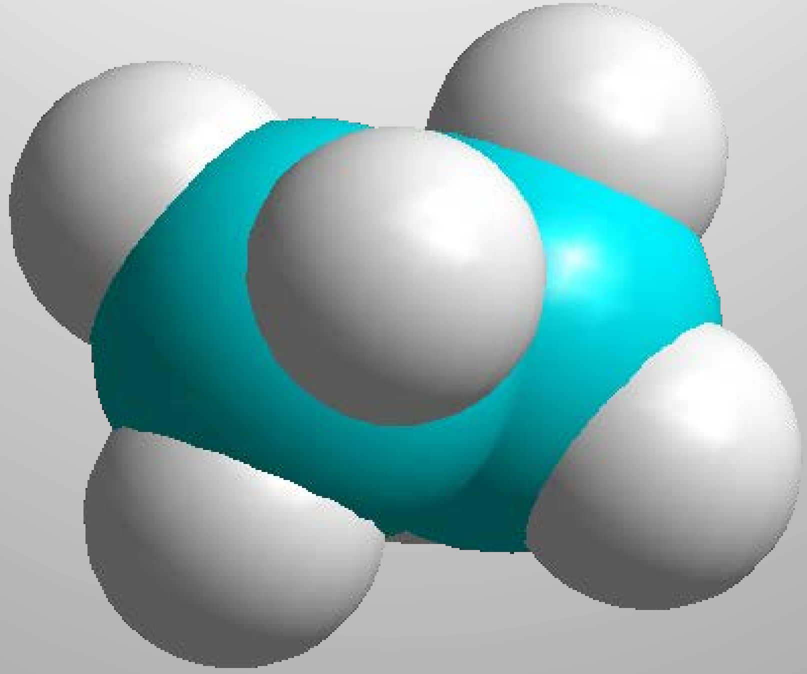
Sticks linking bonded centers of ethane



Balls linked by sticks for ethane



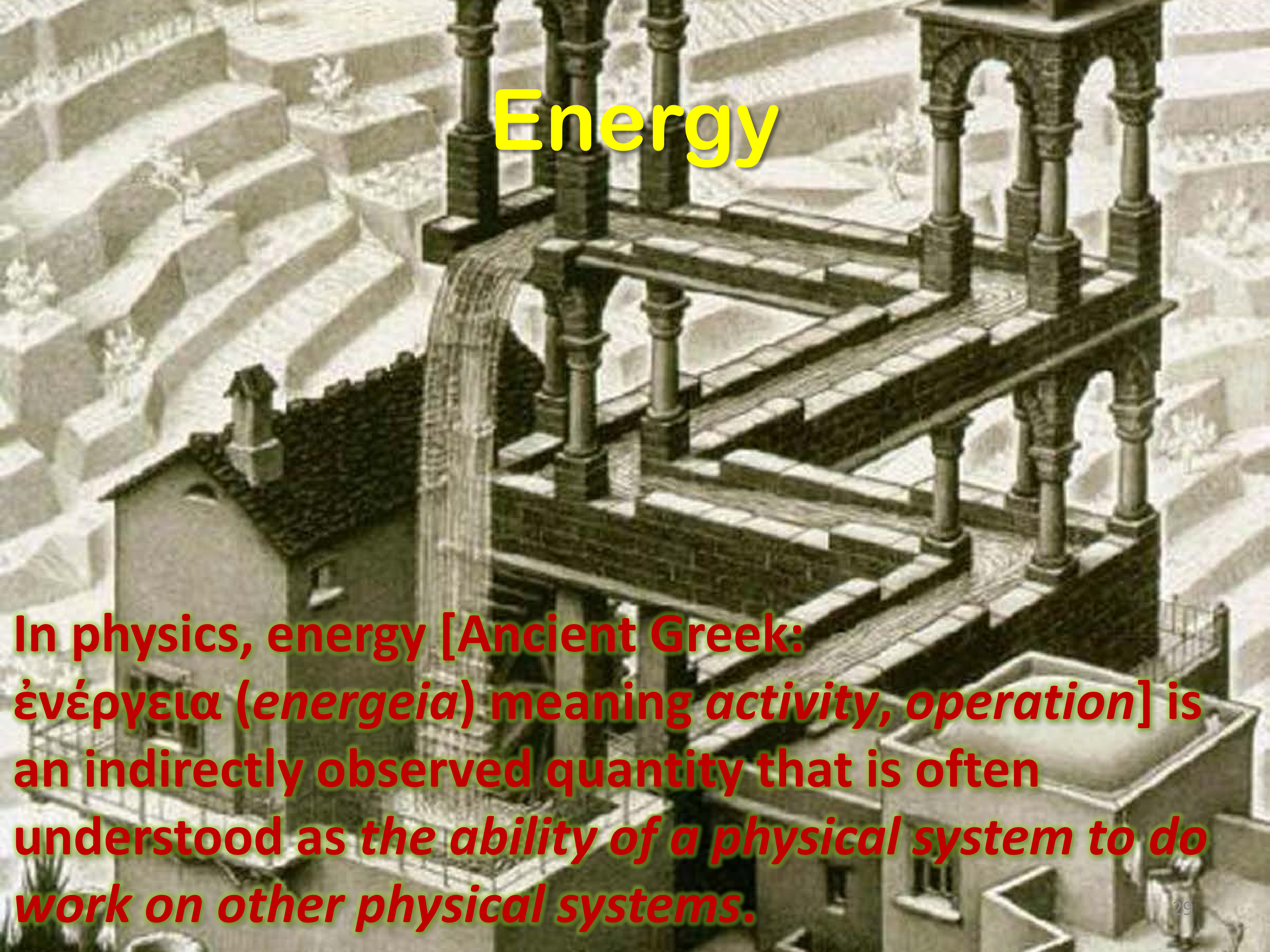
Space filling balls for ethane



Modeling is always present in our day life, in our sciences, in our societies, because we build them sometimes unconsciously for understanding. **It is a way of thinking**.

How to represent a reliable model of nanoworld bodies?

Energy



In physics, energy [Ancient Greek: ἐνέργεια (*energeia*) meaning *activity, operation*] is an indirectly observed quantity that is often understood as *the ability of a physical system to do work on other physical systems.*

The Newton's laws of motion

1. An object at rest will remain at rest and an object in motion will remain in motion at constant velocity unless acted upon by a net force.
2. The net force on an object is equal to its mass times its acceleration ($F = ma$).
3. For every action there is an equal and opposite reaction.

Second Newton's law and modeling nanoscales

Confident models at nanoscales are grounded on the consideration that any system is more stable in conditions of minimal potential energy (or internal energy) where F_i is a force that could change the position of a body at a point $\vec{r}_i$.

$$F_i = m\frac{d^2\vec{r}_i}{dt^2}$$

$$= ma$$

$$= -\frac{\partial E(\vec{r}_i)}{\partial \vec{r}_i}$$

$$= 0$$

Potential energy surfaces

In order to find the most probable molecular structures is necessary a function that expresses the total potential energy, or simply the total energy of the system, in terms of the number and kind of nuclei (Z) and their respective spatial coordinates given by a matrix $\mathbf{R}$, as well as those of electrons:

$$E = E(Z, \mathbf{R})$$

This function is known as the **potential energy surface (PES) of the system** or **hypersurface**.

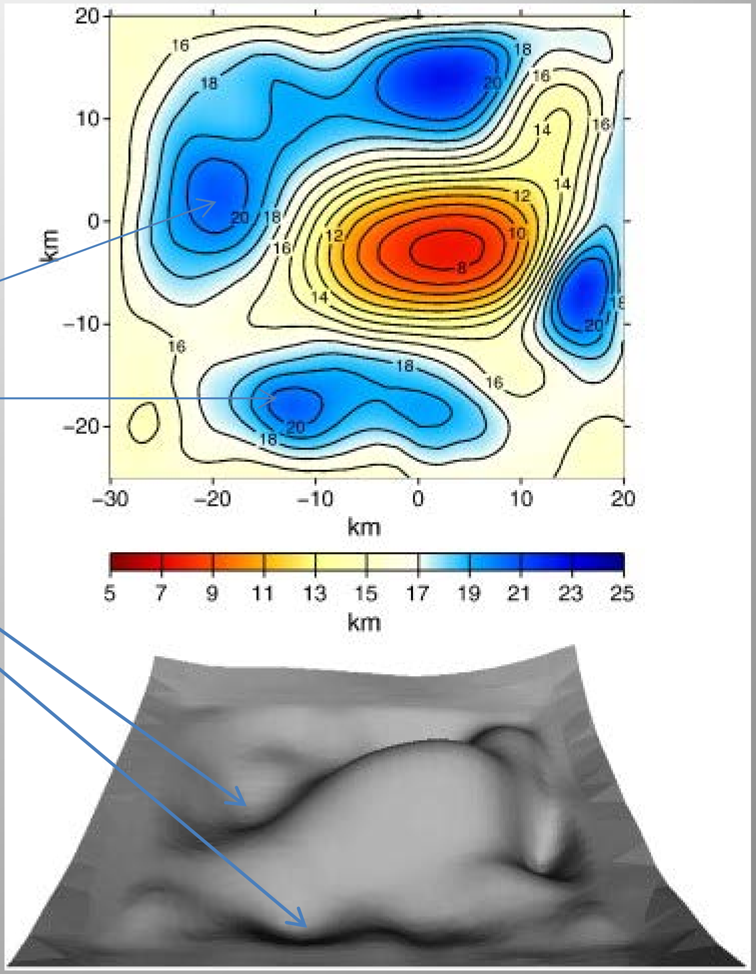
The main problem of methods for modeling nanoscale objects is finding the appropriate analytical or numerical function of such hypersurfaces:

$$E = E(Z, \mathbf{R})$$

An image from earth sciences

Earth sciences can illustrate how behave potential energy surfaces in nanoworld: the energy landscape

Local minima

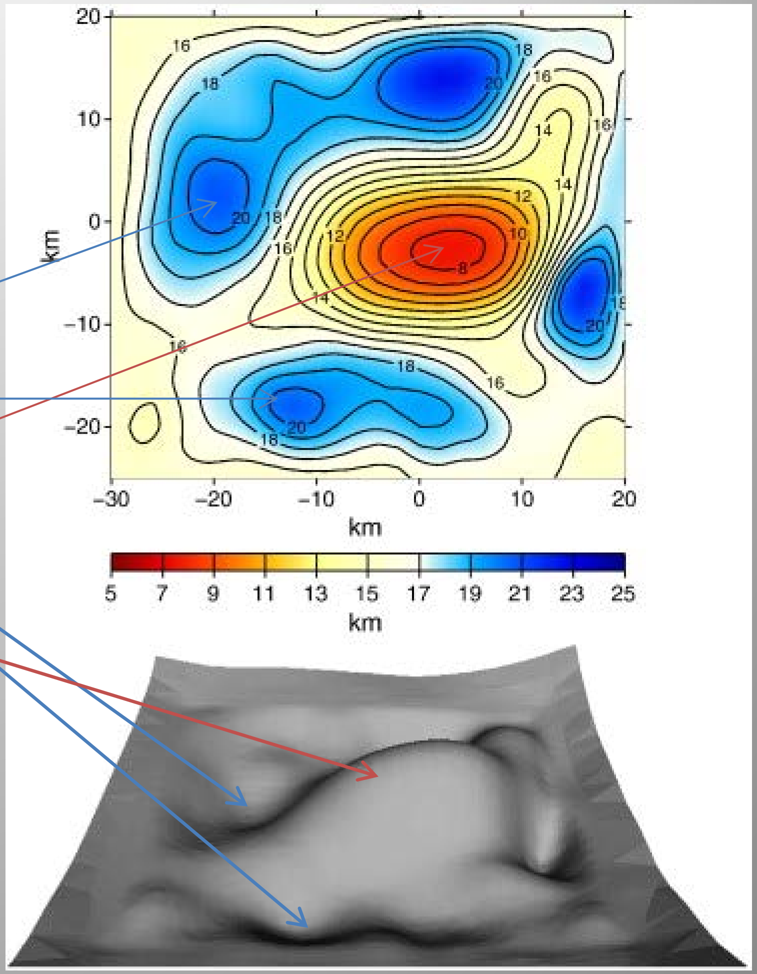


An image from earth sciences

Earth sciences can illustrate how behave potential energy surfaces in nanoworld: the energy landscape

Local minima

Maximum



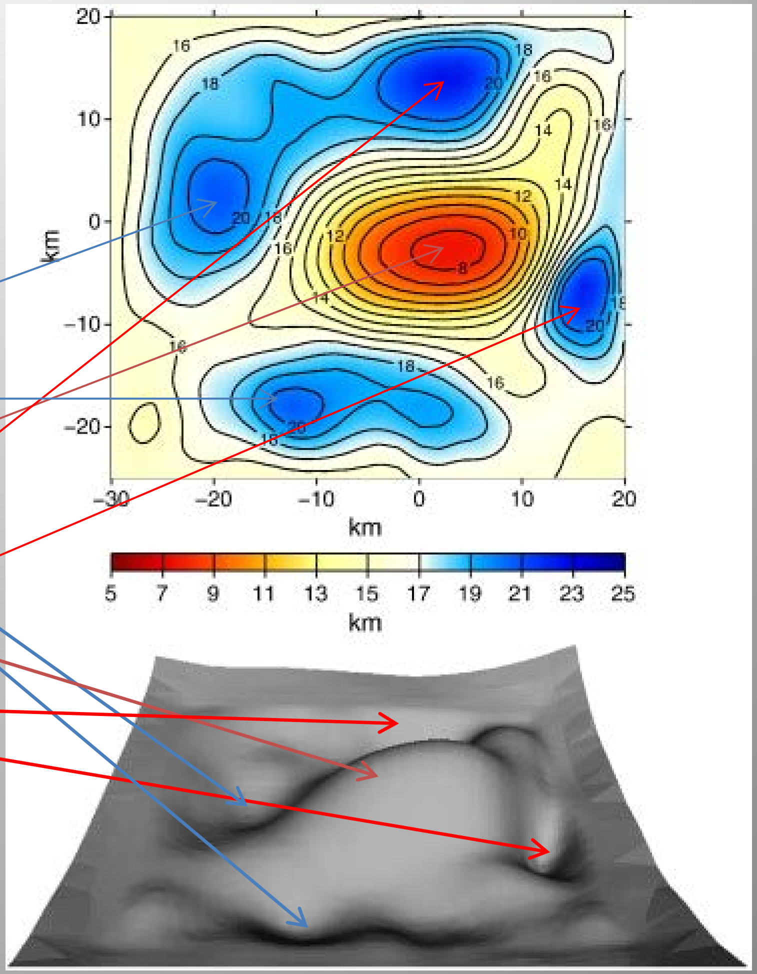
An image from earth sciences

Earth sciences can illustrate how behave potential energy surfaces in nanoworld: the energy landscape

Local minima

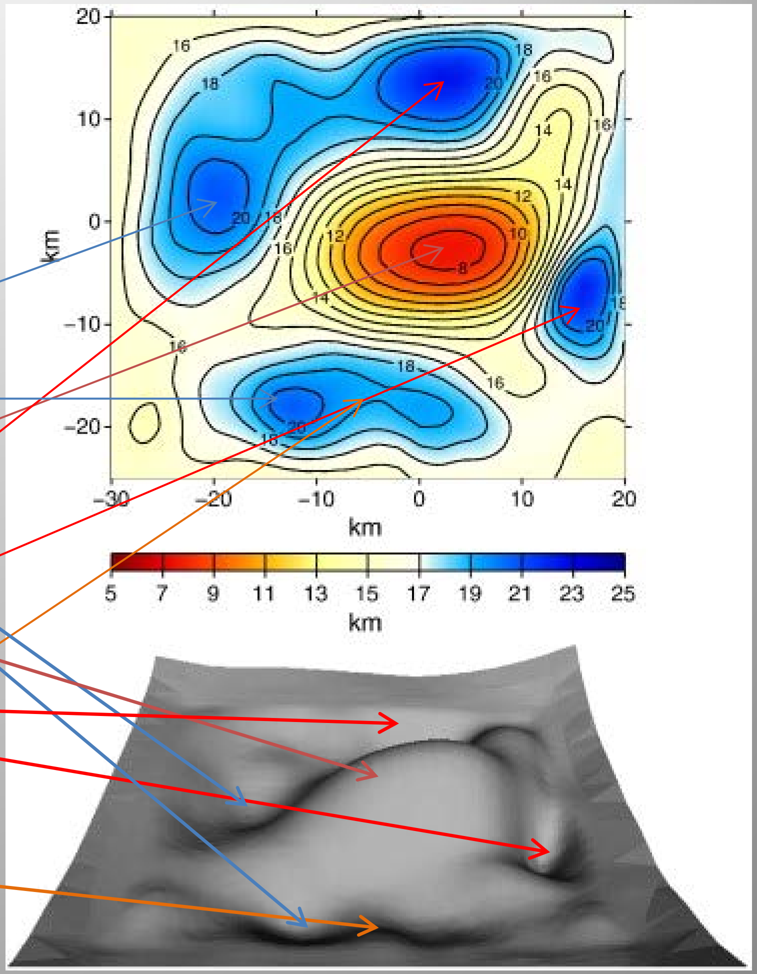
Maximum

Deepest minimum?



An image from earth sciences

Earth sciences can illustrate how behave potential energy surfaces in nanoworld: the energy landscape



Local minima

Maximum

Deepest minimum?

Saddle point

An image from earth sciences

Earth sciences can illustrate how behave potential energy surfaces in nanoworld: the energy landscape

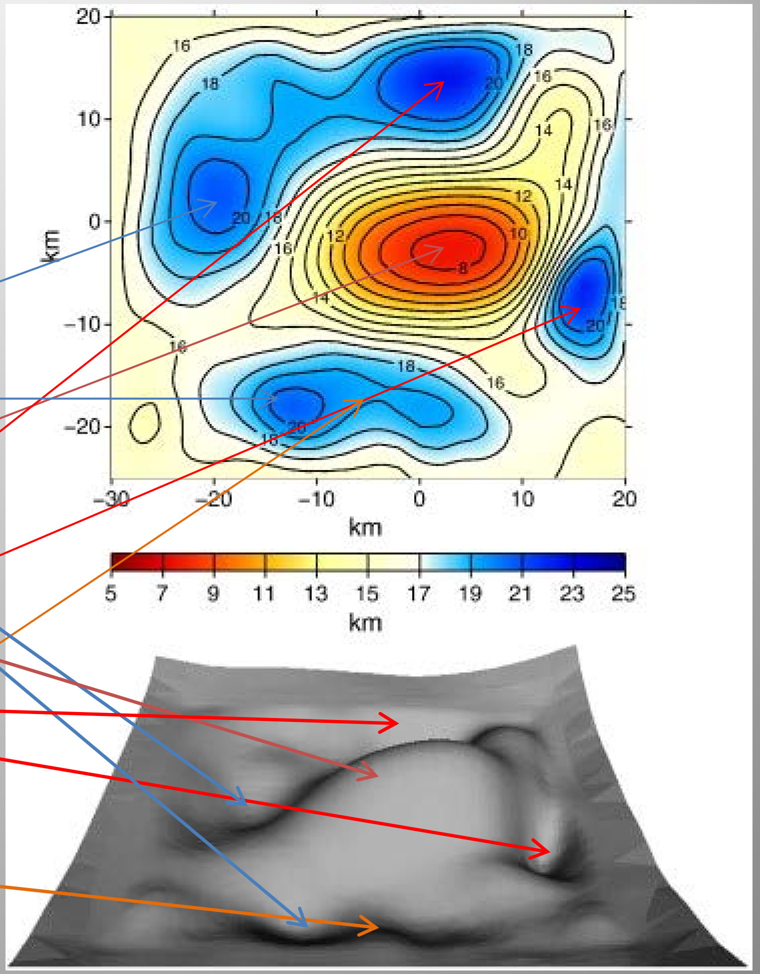


Image from: Prutkin, I.; Vajda, P.; Tenzer, R.; Bielik, M., 3D inversion of gravity data by separation of sources and the method of local corrections: Kolarovo gravity high case study. *Journal of Applied Geophysics* **2011**, *75* (3), 472-478.

A true landscape: Ha-long bay, Viet Nam

Quantum mechanics as a physical theory for nanoscopic systems

Quantum mechanics is the only known theory, until now, providing valid *a priori* results for modeling and describing nanoscopic phenomena, as is the case of molecular interactions and chemical bonding.

Quantum Hypersurfaces for Quantum Models

Quantum models are those where the hypersurface is calculated from *wave functions* associated to the involved particles. It uses to be the most reliable approach to such purpose.

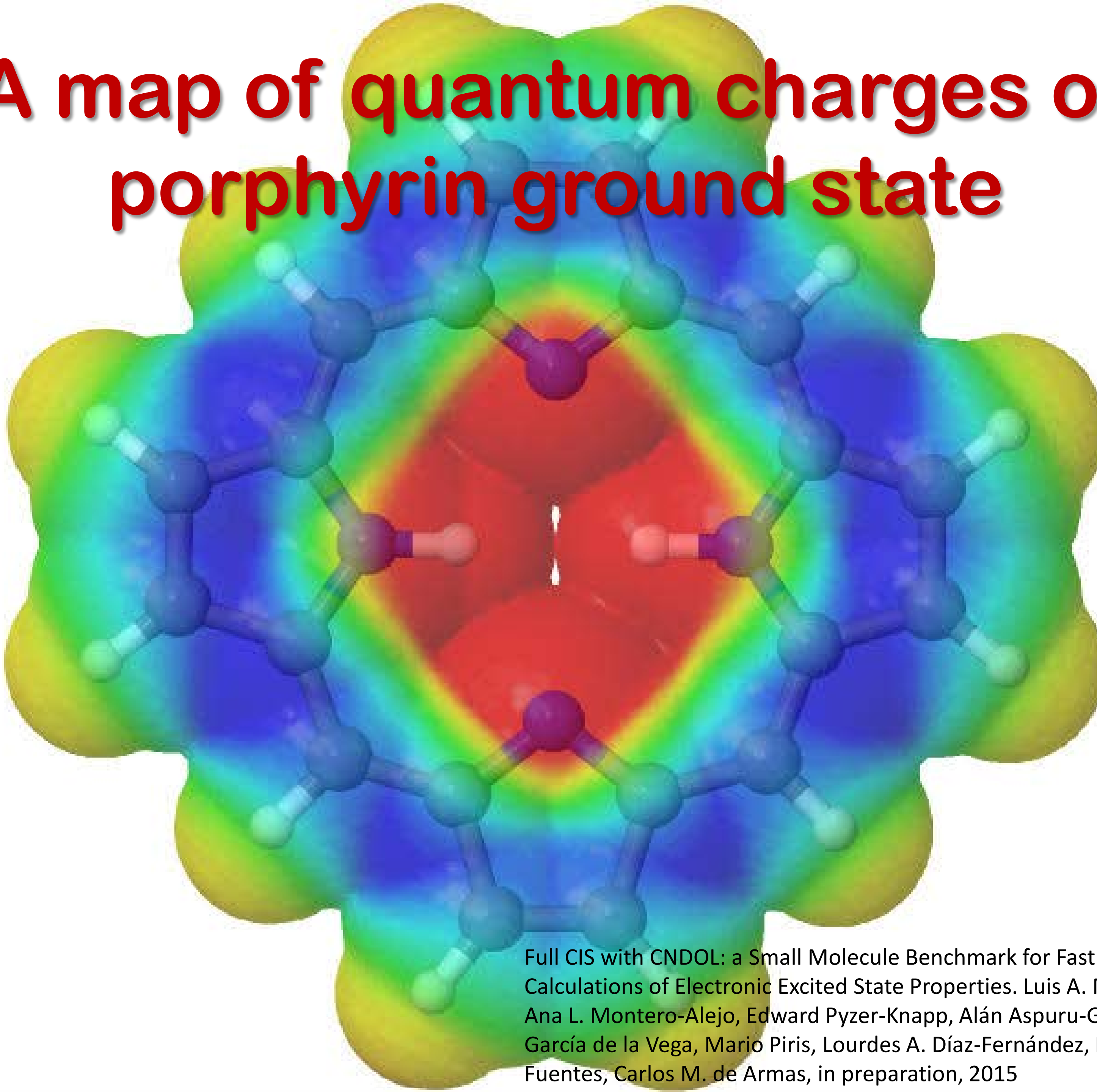
Quantum Hypersurfaces for Quantum Models

Quantum models are those where the hypersurface is calculated from *wave functions* associated to the involved particles. It uses to be the most reliable approach to such purpose.

$$\Psi = \Psi(\vec{r}, t)$$

$$E = \frac{\left| \hat{H}\Psi(\vec{r}, t) \right|}{\left| \Psi(\vec{r}, t) \right|}$$

A map of quantum charges of porphyrin ground state



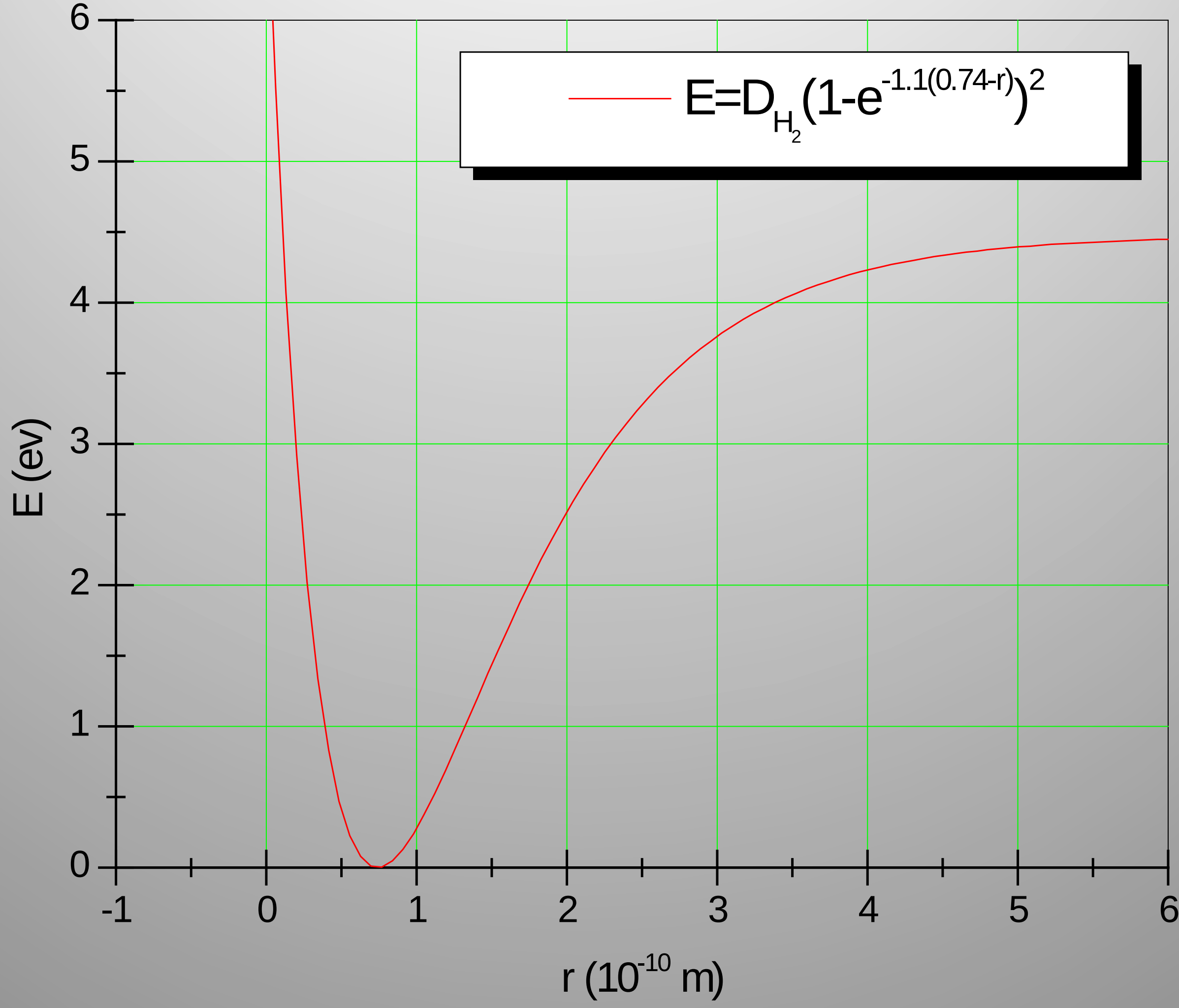
Full CIS with CNDOL: a Small Molecule Benchmark for Fast and Reliable Calculations of Electronic Excited State Properties. Luis A. Montero-Cabrera, Ana L. Montero-Alejo, Edward Pyzer-Knapp, Alán Aspuru-Guzik, José M. García de la Vega, Mario Piris, Lourdes A. Díaz-Fernández, María E. Fuentes, Carlos M. de Armas, in preparation, 2015

“Optimized” molecular geometries

A certain coordinate set $\mathbf{R}_{eq}$ that provides a minimal energy E_{eq} for the whole system is known as the **optimized geometry** and it means a **global minimum of the hypersurface**.

$$\sum_i \frac{\partial E\left(\mathbf{R}_{eq}\right)}{\partial r_i} = 0$$

Hypersurface of H_2 according the Morse's potential



Inventing the concept of energy introduced a way of thinking for understanding facts and processes in our environment.

Inventing the concept of energy introduced a way of thinking for understanding facts and processes in our environment.

It serves as a tool for modeling the whole universe, and even the nanoworld… after quantum mechanics.

Now we know that…

- The way we think was modulated by the scale of the world we live and we develop our common knowledge.

Now we know that…

- The way we think was modulated by the scale of the world we live and we develop our common knowledge.
- A way to understand what happens in other unattainable scale is modeling their structures and related phenomena.

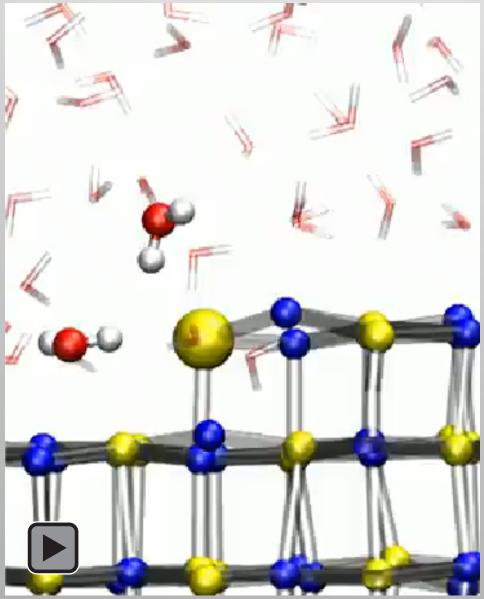
Now we know that…

- The way we think was modulated by the scale of the world we live and we develop our common knowledge.
- A way to understand what happens in other unattainable scale is modeling their structures and related phenomena.
- The concept of energy serves us to find the most reliable structures existing in the nanoworld by applying quantum mechanics, that was designed for it.

Now we know that…

- The way we think was modulated by the scale of the world we live and we develop our common knowledge.
- A way to understand what happens in other unattainable scale is modeling their structures and related phenomena.
- The concept of energy serves us to find the most reliable structures existing in the nanoworld by applying quantum mechanics, that was designed for it.
- Computers can do the calculations needed for such modeling for us.

Molecular dynamics simulation of common salt dissolving in water at a nanoscopic scale



Chloride anions are shown in yellow, sodium cations in blue. The large chloride dissociates from the salt crystal.

http://www.chem.ucl.ac.uk/ice

Group leader
Prof. Angelos Michaelides

University College London
London Centre for Nanotechnology
17-19 Gordon Street London, WC1H 0AH
Tel: +44 (0) 207 679 0647 (Ext: 30647)
Email: angelos.michaelides@ucl.ac.uk

Thanks!